

Vol. 24, No. 2, March-April, 1989

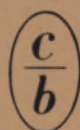
November, 1989

LITHOLOGY AND MINERAL RESOURCES

ЛИТОЛОГИЯ И ПОЛЕЗНЫЕ ИСКОПАЕМЫЕ

(LITOLOGIYA I POLEZNYE ISKOPAEMYE)

TRANSLATED FROM RUSSIAN



CONSULTANTS BUREAU, NEW YORK

LITHOLOGY AND MINERAL RESOURCES

Lithology and Mineral Resources is abstracted or indexed in *Chemical Abstracts*, *Engineering Index*, and *Metal Abstracts Index*.

Lithology and Mineral Resources is a translation of *Litologiya i Poleznye Iskopaemye*, a publication of the Academy of Sciences of the USSR.

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Vol. 23: \$795 (domestic); \$880 (foreign)	Single Issue: \$150
Vol. 24: \$855 (domestic); \$990 (foreign);	Single Article: \$12.50

CONSULTANTS BUREAU, NEW YORK AND LONDON



233 Spring Street
New York, New York 10013

Published bimonthly, consisting of Volume 23 issues 3 through 6 and Volume 24 issues 1 and 2. Subscription price for Volume 23 is \$795, and for Volume 24 is \$855. Second-class postage paid at Jamaica, New York 11431.

Mailed in the USA by Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003.

POSTMASTER: Send address changes to *Lithology and Mineral Resources*, Plenum Publishing Corporation, 233 Spring Street, New York, NY 10013.

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A translation of *Litologiya i Poleznye Iskopaemye*

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Volume 24, Number 2

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The Russian press date (podpisano k pechatii) of this issue was 3/15/1989. Publication therefore did not occur prior to this date, but must be assumed to have taken place reasonably soon thereafter.

SEDIMENTATION RELATED TO TRANSGRESSIONS AND REGRESSIONS
IN AN EARLY TO MIDDLE JURASSIC BASIN OF THE GREAT CAUCASUS

Yu. O. Gavrilov

UDC 552.5:551.762(479)

The influence of transgression and regression on sedimentation in an Early to Middle Jurassic sedimentary basin of the Great Caucasus is considered. The generally transgressive development of the basin was interrupted by regressive intervals, each of which was related to a reworking of previously deposited sediments, creating distinctive sedimentary sequences. The series of regressive episodes is correlated with analogous events in other areas of the world, and is consistent with eustatic fluctuations in sea level.

Thick Lower and Middle Jurassic sandy and argillaceous deposits of the Great Caucasus have quite a complex structure despite a general similarity in lithological composition. Many tens of regional formations are distinguished [20], resulting from changing conditions of sedimentation both laterally and vertically. Analysis of these deposits shows that the specific characteristics of the different parts result from diverse factors, each operating in the Jurassic basin to varying degrees. At the same time the sequence of deposits follows a similar general pattern whether developed in adjacent or widely spread parts of the area. The appearance of each sequence can be related to the same few factors, reflecting a general pattern in the evolution of basin sedimentation. Some of these patterns are related to transgressive and regressive phases in the development of the Caucasus basin. This paper attempts to evaluate the possible influence of these factors on the accumulation of this sedimentary rock mass.

As a result of research conducted on the Jurassic sediments of the Great Caucasus, it has been established that a gradual widening of the Caucasus basin occurred during part of the Early to Middle Jurassic (Fig. 1) [4, 16, and others]. One of the principle causes of transgression was the onset of intensive downwarping of the basin floor, which brought about the accumulation in its axial zone of many kilometers of sediment. Through time the area of subsidence spread, while the sea correspondingly encroached over a wider area. It should be taken into account that the Caucasus basins were a part of Tethys, for which a series of eustatic fluctuations covering the Jurassic period have been established. Eustatic sea level variations were therefore also expressed in the Caucasus region. The combination of these factors, comprising the genuine basin subsidence of the Caucasus troughs together with the eustatic fluctuations of the Tethys sea operating over a wide area, gave a nonuniform character to the transgressions, which in turn influenced to a considerable extent the accumulation of sediments.

The movements of the coastline through time, i.e., the transgressive and regressive episodes, influence the nature of sediment input to the basin. By controlling the accumulation of sediment on, or abandonment of, fluvial deltas and submarine canyon systems, they caused the sedimentary depocenter to shift, sometimes causing the redistribution of large masses of sediment. It was this which was responsible for the relative complexity of the fabric of the J_{1-2} (Early to Middle Jurassic) terrigenous complex. Related to this very important discussion of the original nature of the sediments in the Great Caucasus geosynclinal flexure is the question of how the Early and Middle Jurassic transgressions developed.

The best locations for examination of this question appear to be in the Jurassic sediments of the northern Caucasus, and especially in its central region where the fauna are best described and where they are sufficiently precise to trace the relationships between the sedimentary complex. Accordingly, since these aspects were most important to us, the

Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 3-15, March-April, 1989. Original article submitted July 11, 1988.

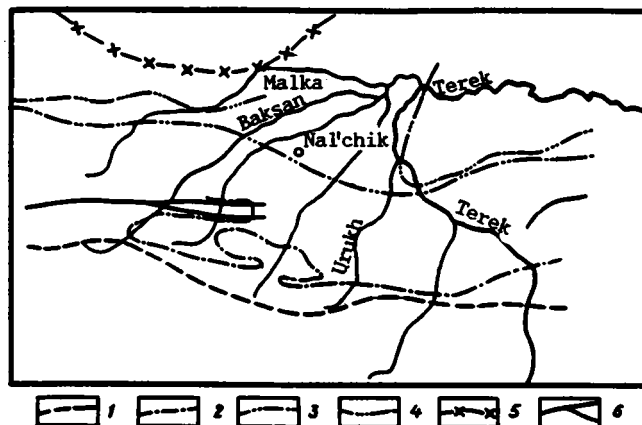


Fig. 1. Distribution of marine Lower and Middle Jurassic deposits of the Central Caucasus [16]. The limits of sediment distribution: 1) Sinemurian-lower Pliensbachian; 2) Upper Pliensbachian; 3) Toarcian; 4) Aalenian; 5) Upper Bajocian; 6) Tyrnyauz-Pshekishsk suture zone.

material analyzed was primarily from the northern part of the Caucasus sedimentary basin. Nonetheless, data from other regions of the Caucasus either confirmed or at least appeared to us not to contradict the conclusions drawn.

TRANSGRESSIVE STAGES OF BASIN DEVELOPMENT

One might expect to find particular features which characterize the Early and Middle Jurassic transgression in the Caucasus region. As a result of studies of the Jurassic sedimentary stratigraphy up to the present, it has been possible to amalgamate the numerous and varied local formations into a large-scale regional framework of horizontal stratigraphic subdivisions [16, 18, and others], which corresponds to definite stages in the development of the sedimentary basin as a whole.

The initial stage of development of the geosynclinal downwarp was marked by the formation of deposits of the Svanetsk Formation [18], of Hettangian(?)–Sinemurian to early Pliensbachian age. The accumulation of mainly coarse sediments occurred during shallow-water conditions in the basin. The base of the Svanetsk Formation in different regions is not of the same age but ranges from the lowermost Sinemurian (Hettangian?) in the axial part and on the southern margin of the downwarp, to the lower Pliensbachian on the northern margin of the geosyncline and on the southern part of the Scythian plate. Poor faunal characterization of the sediments from this formation unfortunately hampers any clarification of the processes by which the transgression developed at this stage.

Note also that the transgression, having begun in the latest Hettangian(?)–basal Sinemurian, proceeded irregularly, so that the Svanetsk Formation is of varying extent in different areas [18]. From the changing age of the base of the Veriyutsk Formation it may be stated that the broadening of the basin and opening up of new areas of sedimentation occurred in the first half of the late Sinemurian, and the basal Pliensbachian.

In contrast to the base of the Svanetsk Formation, its top is characterized by a quite clearly pronounced transition into the overlying deposits, which are generally of a different composition (the Tsiklaursk Formation). The mainly argillaceous sediments of the Tsiklaursk Formation (upper Pliensbachian–lower part of the lower Toarcian) [16, 18] are distributed over a wider area than those deposited earlier. With the onset of this stage a broadening of the basin began, with a marked deepening of its central area where comparatively thin sediments started to accumulate. The nature of the transgression can be discerned from features of the upper Pliensbachian (Domersk) sediments of the central region of north Caucasus. In some places here (the Uruk River Basin) a series of sections in the Domersk deposits may be observed, ideally aligned across the Caucasus strike direction. Analysis of their structure shows that at the boundary between the early and late Pliensbachian the sea rapidly advanced at least some tens of kilometers to the north. As a result, comparatively shallow-water sediments typical of a shelf accumulated in this region.

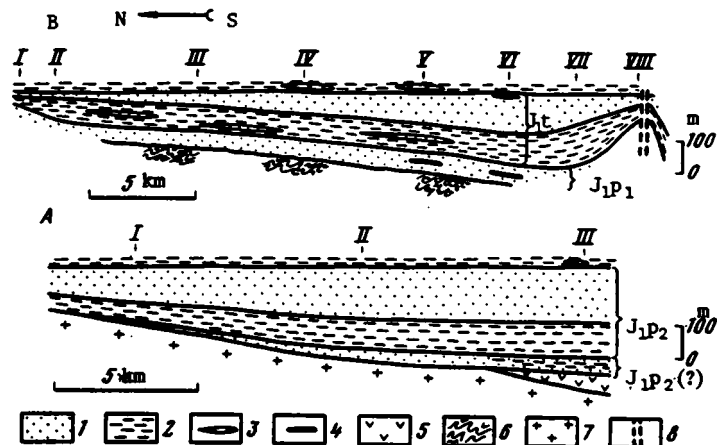


Fig. 2. Cross sections of sedimentary bodies accumulated on areas of a shelf: A) in late Pliensbachian time within the Digoro-Osetinsk SFB; B) in the second half of the early Toarcian and late Toarcian time. 1) Sandy deposits; 2) argillaceous and clay-silt deposits; 3) lenticular beds with iron-rich oolites; 4) coal beds; 5) volcanogenic bodies; 6-7) pre-Mesozoic basement formations [6] crystalline slates; 7) granites and granite gneisses; 8) Tyrnyauz-Pshekishsk suture zone. Roman numerals indicate the locations of the sections. Section A: I) Fasnal; II) Farskat; III) Lezgor. Section B: I) Malka (Gedmysh); II) Gorallykol; III) Western Kandzhal; IV) Tyzyl (Bardyrlykol); V) Tyzyl (Tashlysyrt); VI) Baksan; VII) Gitche-Koshtansy; VIII) Khasty. Thicknesses from [4] and others.

Moreover, sedimentary conditions over the area were characterized by uniformity and stability.

The accumulation of sediments of the Kazbek Formation (upper part of the lower Toarcian-upper Toarcian [18]) also began with a rapid advance of the sea to the north, flooding the southern part of the Scythian plate, which began to act as a shelf. At this time, the Digoro-Osetic structural-facies belt (SFB)* was transformed into a continental slope. The lower boundary of the Kazbek Formation (Dzhigiatsk Member) within the Labino-Malkinsk SFB has been dated as the base of the *Hildoceras bifrons* ammonite zone. However, data obtained more recently shows that it passes down into the *Harpoceras falciferum* zone [11], which must accordingly be the age of the boundary between the Tsiklaursk and Kazbek Formations. A new transgressive stage may therefore be considered to have begun in the middle of the early Toarcian. Just as in Domersk time, after a rapid advance of the sea to the North the area of newly formed shelf began a period of relatively stable sedimentation. Moreover, in both cases the distribution of sediment bodies on the shelf was broadly similar, beginning (after the formation of thin basal beds of sand and gravel) with deposition of clays and silts which subsequently gave way to sandstones deposited on a shallow water shelf. Figure 2 shows the structure of these sediment bodies, which accumulated on shelf areas in Domersk time in the Digoro-Osetinsk SFB, and the latter half of the early Toarcian-beginning of the late Toarcian in the Labino-Malkinsk SFB. They can each be seen to have developed in a similar way and with similar facies. The rate of transgression is through to have been high, since on the whole the same conditions of sedimentation were established across the whole area of the shelf. Moreover, the fairly consistent thickness of the lower part of the transgressive series shows that substantial peneplanation occurred to the land before flooding occurred. The pulsatory character of the transgression recognized by some workers [3 and others] should be noted. Advance of the coastline toward the north caused the flooding of river deltas flowing into and supplying sediment to the basin. The rise of the erosive base level slowed down the denudation of the land. Rivers must have deposited large amounts of detrital material in flooded river valleys and simultaneously along the coast. The deeper

*According to the structural-facies subdivisions described in [16, 18].

parts of the shelf accumulated thinner argillaceous deposits, sometimes with sandy and silty material. Later, extensive sedimentary deposits accumulated on the shelf with a corresponding reduction in water depth, as newly active deltas began to deliver sandy material to the shelf, helped by wave activity and longshore-drift. Moreover, at this stage of sedimentation the hydrodynamic activity was sufficiently high to produce well-sorted deposits. Argillaceous debris was carried out beyond the shelf into the deeper marine area where, for example in Domersk time, shale facies accumulated in the Tsiklaursk Formation and, in the Toarcian, the Ardonsk Formation.

The deposits of the Anchkhoisk Formation (Aalenian-lowermost lower Bajocian [18]), and in particular the upper Aalenian deposits of north Caucasus and Ciscaucasus, are the most widely distributed. The late Aalenian is marked by one more transgressive episode, when the sea drowned on extensive area of northern Ciscaucasus. Here, and in more western regions of the Labino-Malkinsk SFB, whatever deposits formed at the time, they all show signs of having been deposited in quite shallow water. The highest (regressive) part of this formation is replaced by siltstones, sandstones, and lenticular bands of bioclastic limestone [16, 18]. Accumulation of sediments of the Anchkhoisk Formation was interrupted by a regression at the end of the Aalenian-beginning of the Bajocian.

Beznosov [3] consider that the early Bajocian transgression commenced not later than the end of the "Sonninia" sowerbyi zone, and reached its maximum during the Stephanoceras humphriesianum zone. Only in some elevated areas of Dagestan do lower Bajocian deposits (Kumukhsk Formation [3, 18]) lie without any apparent discontinuity on the Aalenian; in the remaining parts of north Caucasus the sediment bodies of lower Bajocian age lie transgressively on all underlying deposits, and correlate with the two highest zones of the lower Bajocian. The lower zone at the base of the Bajocian falls within the period of the disconformity [3]. The early Bajocian stage ended with a brief regression.

At the beginning of the late Bajocian a new transgressive event advanced the sea further to the north and deposited late Bajocian and early Bathonian sediments (Tsudakharsk Formation [3, 18]) which overlapped the Dobaioosk Formation [3, 4, 9, and others].

It is considered here that the Tsiklaursk, Kazbek, and Anchkhaisk Formations formed as a single entity rather than as an interrupted series of sediments, united in the Sebel'dinsk Group, which persisted during one large-scale process of geological development of the Great Caucasus [18]. It seems to us that this is the most likely location of the central part of the Jurassic sedimentary basin, and a more detailed picture of the nature of the development of the Sebel'dinsk Group is revealed in its regional parts: a general transgressive development of the basin, complicated by periods when the sea retreated. These periods, in our view, preceded stages of rapid transgression of the sea, and correspond well with the boundaries between formations. We shall examine these periods, and it is convenient to begin with an episode confined to a brief interval on the boundary between the Toarcian and the Aalenian.

REGRESSIVE STAGES IN THE DEVELOPMENT OF THE CAUCASUS BASIN

The generally transgressive development of the Caucasus basin is confirmed by numerous data. However, the emergence within thick (7-8 km) marine deposits over a wide area of northeastern Caucasus (Dagestan) of a complex of deltaic facies (Karakhsk Formation [24] or Batlukhsk and Datunsk Formations [6]), which are in places coal-bearing, may demonstrate the existence of a regressive stage complicating the general tendency toward broadening of the basin. The question arises as to whether it is possible to determine if this is a local or more widespread occurrence.

The quantity of sediment in deltaic deposits is considerable. Frolov [24] has measured the surface area of the Volga delta as 20,000 km², and the sediment thickness reaches 1.5 km or more. The volume is therefore enormous. Frolov relates the delta progradation toward the sea to uplift of the land on the north of the Caspian. In the case under consideration the regression might have had a local cause, but at the same time it was able to bring about a widespread regression. On account of the lowering of the erosive base level, sediments (chiefly sandstones) which had accumulated earlier in coastal areas of the land and the shelf were eroded and redeposited on the continental slope. This resulted in an area of sediment accumulation at the end of the late Toarcian-early Aalenian.

It is evident that traces of a regression and signs of a decrease in water depth would be best developed in areas of relatively shallow-water sedimentation. During this period a quite considerable area to the west of the region formed a marine shelf. This had developed in a Toarcian-Aalenian basin within the southern part of the Scythian platform, as noted above, during the early Toarcian as a result of the transgression.

Bezborodov [2] conducted extensive lithological research into the Lower and Middle Jurassic deposits within central and western Caucasus, and showed that variation in the Toarcian rock succession demonstrated a shallowing of the sea at the close of Toarcian time. He related this occurrence to uplift at the end of the Toarcian. Rostovtsev and Nikanorova agreed with this for the western Caucasus, and noted that the lower Aalenian beds lie with minor erosion on the upper Toarcian [22]. Having noted that there is a tendency for uplift at the end of the late Toarcian-early Aalenian both in the eastern and western parts of the area, it is possible to state quite confidently that a widespread regression affected the whole of the North Caucasus.

In some of the most northerly sections of J_{1-2} near the former coastline (River Rakasezen), and where the signs of regression are most likely to be expected, the lack of fauna characteristic of ammonite zones Dumorteria pseudoradioza and Leioceras opalinum [4] may clearly be interpreted as indicating a break in sedimentation at this time.

Study of the J_{1-2} section shows that certain specific types of sedimentary formation are concentrated around the top of the upper Toarcian to lower Aalenian interval. An example of such a distinctive lithology is provided by the concretionary conglomerates or "intraformational discontinuities" [2, 4, 5, and others]. They occur as beds formed, as a rule, of diagenetic concretions which are often somewhat rounded, together with wood fragments, mud clasts, shells of ammonites, bivalves, gastropods, and belemnite rostra. The components of these beds tend to be highly disordered. These formations are generally developed in subaqueous conditions, as a result of submarine erosion of sea-bottom sediment. Thin beds of argillaceous material are removed, with the accumulation of various coarser components, including concretions, shells, etc. The presence of these concretionary limestones requires very active hydrodynamic conditions to have operated in relatively shallow water. In the lower parts of the Baksansk beds (Toarcian-Aalenian) these beds are particularly common. In the Tyzyl River section, for example, they occur every 1-2 m [5]. In under- and overlying deposits they occur much less frequently.

Oolite-bearing iron-ore formations are the most common lithology at this stratigraphic level. The thickness of these formations is from a few tens of centimeters to 1 m. In some sections they occur as four or five relatively thick beds, separated by layers of claystone. Often, iron-ore formations pinch out within a distance of a few hundred meters to a kilometer, so that they are absent in adjacent formations. Oolites are formed primarily of goethite or hydrogoethite. Chamosite is less widely distributed, but predominated in the paragenesis of oxide minerals. It should be noted that many of the iron-ore beds have a brecciated structure, and that they contain concretions washed out of argillaceous sediments, in addition to numerous shelly remains.

The majority of workers have shown that the origin of iron-ore formations in central Caucasus has been from iron entering the basin from the weathering products of the Malkinsk and other serpentine-rich massifs. Originally, the iron concentrated by settling in an area close to the source. In the sediment it developed into an oolite, which was evidently primarily of iron-silicate composition. Subsequently, the sediment was eroded and redeposited on the shelf in the south of the basin [5]. In the process of redeposition of the oolites, authigenic mineral oxides formed, which were not present originally. The most likely reason for this erosion of sediment is, in our view, the lowering of sea level during a regression, and the seaward withdrawal of sediment accumulations from the hydrodynamically active zone by wave action.

Hallam and Bradshaw [33], working on diverse transgressive and regressive sedimentary formations of comparable age, came to the conclusion that oolite-bearing iron-ore formations are reliable indicators of regressive episodes. Our observations on the distribution of iron-ore beds in deposits J_{1-2} of the Great Caucasus agree completely with this conclusion.

In parts of the basin more remote from the shore, it would be expected that signs of a drop in sea level would be harder to recognize. However, even here some indications of a change in sedimentary conditions are present. In the deposits of the continental slope (in Digoro-Osetinsk zone) in the higher part of the upper Toarcian and lower Aalenian, "concre-

tionary conglomerates" appear, although in much smaller amounts than on the shelf. More interbeds of silty claystones and sandstones are present, compared to the thinner deposits of underlying formations. All this indicates a strengthening of the hydrodynamic regime in the basin, which allowed the transport of coarser sediment.

Data on the make-up of sedimentary successions on the southern slope of the Great Caucasus also demonstrate the existence of regressive stages in the basin development. Chikhradze, who studied the Lower and Middle Jurassic deposits of the southern slope, concluded that at the beginning of the Toarcian much the same sedimentary conditions prevailed as in the Domersk, but subsequently the regression of the sea began, and sedimentary conditions became correspondingly more complex [28]. In addition to an increasing content of the sediment in the southern part of the Toarcian-Aalenian sedimentary tract, intraformational erosion surfaces are also found, as well as lenticular beds of pebbles formed from local rocks (clay shale, carbonate concretions, etc.), which indicate deposition in rather active hydrodynamic conditions.

Chikhradze linked the lowering of sea level to crustal compression leading to Toarcian-Aalenian uplift. The timing of uplift could quite clearly be taken back as far as the early Toarcian, as it affected sedimentation in the Domersk, while by the late Aalenian there was already evidence of deep basins and marine transgressions (as evidenced by deposits in Svanet and Gornoi Rache). It is thought most likely that the period when the sea level was lowered in the southern part of the geosynclinal flexure occurred in the late Toarcian to early Aalenian, i.e., during exactly the same time interval as the lowering of sea level in the North Caucasus.

In the more southerly regions of Transcaucasus, Toarcian-Aalenian deposits are exposed on the Dzirulsk massif, and also in the cores of some anticlines. On the Dzirulsk massif, the lithological composition of the sediments (biogenic red limestones) and their poor faunal characterization do not permit the zones of interest to us to be distinguished for analysis. At the same time it should be noted that on the northern edge of the massif, condensed deposits are observed in the upper part of a sequence of terrestrial sediments. This is connected with regression of the sea on this tract [15]. Kakhadze considered the beginning of the transgression to have taken place in the early Aalenian.

Out of the other places where J_{1-2} deposits outcrop, only in the area of the Loksk massif are they well characterized faunally. Here, in primarily argillaceous-silty sections of the upper Pliensbachian to Aalenian interval which correspond to the lower Aalenian, is a clearly visible increase in the content of sandy material [17]. It seems to us that in this area, such an increase in the content of coarser material within the section may also demonstrate the lowering of sea level at the end of the late Toarcian-early Aalenian time.

The stratigraphical break established by Drobyshev [7] and Shikhalibeili [29] in the Kurushsk region of Azerbaidzhan could clearly be considered to be a reflection of the same geological event in the Great Caucasus. Here, the absence from the J_{1-2} section of sediments corresponding to part of the upper Toarcian is observed, and the Aalenian transgressively overlies the older rocks. Besides this, Agaev [1] noted that coarse-grained, sometimes arkosic, material accumulated in the Azerbaidzhan region simultaneously with the formation of the Karakhsk Formation on the southern side of the sea.

As we have seen, over almost the entire territory of the Caucasus, wherever at the end of the Toarcian and beginning of the Aalenian a lowering of sea level may have affected in some degree the composition or structure of the sediment, it has been possible to find traces of this influence. Examination of the data has allowed us to judge quite confidently the existence at this time of a comparatively short-lived but distinctive regressive phase in the development of the Caucasus basin. The fact that traces of regression appear in diverse regions of the Caucasus suggests that this phenomenon was a reflection of a much more widespread process - a eustatic lowering of sea level. In fact, in regions adjacent to the Caucasus, for example in Bulgaria, the Toarcian-Aalenian boundary is connected with a break in sedimentation [27]. The fact that the Middle Jurassic deposits overlie the Toarcian along an erosional surface in most parts of the Crimea [23] is also consistent with this hypothesis. The general conclusion drawn from information on the lithology and stratigraphy of Jurassic deposits from various parts of the world has led Vail et al. [34] and Hallam [25, 31] to the conclusion that breaks in sedimentation are very widely distributed on the Toarcian-Aalenian boundary. These workers estimate the magnitude of the eustatic fall in sea level to have been a few tens of meters.

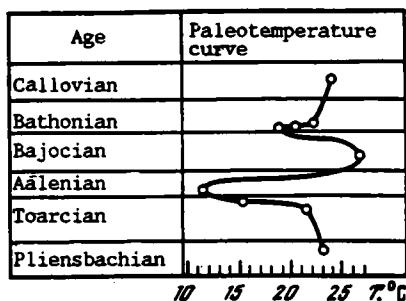


Fig. 3. Paleotemperature curve for Early and Middle Jurassic time in the northern Caucasus [19].

Lowering of sea level can be shown to have had effects which might not immediately be considered to be linked with eustatic fluctuations. Thus, for example, Rostovtsev, considering the paleobiogeography of the Early and Middle Jurassic of the Caucasus basin, noted that a generally mixed ammonite fauna was widespread. That is, forms characteristic both of the mid-European province (NW Europe) and the Mediterranean occurred [21]. However, during the Toarcian (and particularly in the late Toarcian and Aalenian) the mid-European element increased. Ammonoids of mid-European aspect penetrated northern Caucasus, and then further south, apparently through the Danish-Polish and Preddobrudzinsk flexures [15, 26], and not from the seas to the south. There was therefore a marked deterioration in the connection with the basins of southern Europe at this time. The probable cause of this deterioration may have been the lowering of sea level, and the appearance in the shallow-water peripheral parts of the basin of a system of islands, bringing about a partial isolation from the Mediterranean.

The end of the Toarcian and beginning of the Aalenian was also unusual for the Jurassic because of a temperature anomaly. Research by Yasamanov has demonstrated that in the northern Caucasus and northern Transcaucasus the marine temperatures, established from belemnite rostra, were ~20-22°C in the early Toarcian, whereas in the late Toarcian they had fallen to 15-17°C. In the early Aalenian of western Transcaucasus, the temperature obtained is ~7.2°C; while on the west of the north Caucasus it is 11.9-12.2°C. Later, the temperature began to increase, and by the close of the late Aalenian it had reached 22.5°C [30]. The tendency toward a lowering of temperature at the end of the Toarcian is confirmed by palynological data. The content of thermophilic forms, such as the cheirolepids, also declines abruptly at this time [19]. Figure 3 is a plot of temperature variation for the northern Caucasus in the Early and Middle Jurassic. It can be seen to agree quite closely with the supposed lowering of sea level in the late Toarcian to early Aalenian. Yasamanov [30] noted that the lowering of temperature in the early Aalenian also occurred in some more northern regions of Eurasia, such as Northern Siberia, central regions of the European part of the Soviet Union, and elsewhere. The temperature minimum in the Caucasus coinciding with the marine regression may have been related to a change in the hydrological regime of the basin. The onset of a system of currents brought the colder waters of northwest Europe a long way to the south, and these may have followed the same route by which the penetration of mid-European ammonoid forms occurred. Unfortunately, there is at present no reliable information on the water temperature of northwest European basins. Results of some researchers (Bowen, Fritz) give quite high temperatures for these basins, but these have been criticized as being excessive [13] for reasons which we find convincing. But even if this explanation for the lowering of water temperature in the Caucasus were not confirmed in some way, the coincidence of the time of its occurrence with the regressive episode could hardly be by chance. They must have some causal relationship, which further research could explain.

In the Liassic, a lowering of sea level occurred at the beginning of the early Toarcian [3, 4, 12]. At this time in some parts of the northern Caucasus a break in sedimentation is noted in Jurassic rocks. Thus, in a section of the Eastern Balkarsk SFB, deposits corresponding to the *Dactylioceras tenuicostatum* and part of the *Harpoceras falciferum* ammonite zones are absent. A similar picture is observed in the western part of the Arkhyz-Gyzerip'sk SFB. In the Eastern Balkarsk SFB, which had previously been characterized by coastal sedimentation, a lowering of sea level caused a retreat of the sea toward the South, so that sedimentation stopped. In the western part of the basin, sediments of this age are absent near the region of the Tyrnyauz-Pshekishsk suture zone, but to the north and south sedimentation continued. The break in sediment accumulation is connected, apparently, on the one hand, to the suture zone which formed a relatively high area of the basin and, on the other

hand, to the formation in places of lenses of shallow-water biogenic limestone. With a lowering of sea level, the sea withdrew from relatively high areas, causing deposition to stop.

In the deeper marine parts of the basin at this time, the deposition of the argillaceous Galiatsk Formation occurred. The boundary between this and the overlying, also argillaceous, deposits can be clearly distinguished. In the Galiatsk Formation are packets of claystone containing intricately structured concretions formed in sediments bioturbated by mud-eaters. A distinctive bed (1-1.5 m thick) of gray claystone is penetrated by numerous small gypsum-infilled fractures, and contains limestone lenses (0.5 × 1.5-2.0 m) with a biothermal appearance. Formation of this bed is related to a rapid shallowing of the water, and to subaerial weathering of argillaceous mudstones. This led to the dehydration and cracking of the sediments, and the oxidation of diagenetic sulfides by meteoric waters, resulting in the generation of gypsum. In the Galiatsk Formation a carbonate bed up to 1 mm thick and containing iron-rich oolites occurs [8]. This further demonstrates the shallow-water and unstable sedimentary conditions noted above. The nature of sedimentation in the Galiatsk Formation is a reflection of the same phenomenon: the lowering of sea level at the start of the Toarcian.

Direct observations of signs of sedimentary breaks of this age are not at present known to us from other regions of the Great Caucasus. However, the following circumstances should be noted. In a section of the Ratlubsk Formation from Dagestan dated as lower Toarcian [6], an interval from the argillaceous lower part of the formation consists of lenses and thin interbeds of conglomerate, which are not seen in the over- and underlying deposits of a similar age. The appearance of conglomerates seems to be related to the retreat of the sea, and increased erosion of the land to the northwest.

One further episode of lowering of sea level can be clearly recognized from the Liassic, at the close of the early Pliensbachian. At this time deposition of the Svanetsk Formation ended, in the upper part of which occur lenses of limestone or marble. In parts of the highest beds of the Svanetsk Formation, condensed sedimentary packets contain ammonites all of lower Pliensbachian and even upper Sinemurian age [18], demonstrating that at least local erosion of earlier-formed sediments occurred. Unfortunately there are at present no reliable geological or lithological data which would allow regressive episodes to be recognized in Sinemurian basin development, although judging from the structure of sediment bodies in other regions at this time, episodes of eustatic lowering of sea level also occurred here [31, 32].

In the Middle Jurassic, a regressive stage in basin development is known from the topmost Aalenian-basal Bajocian (sowerbyi zone, [3, 10, and others]). Breaks in sedimentation are seen virtually everywhere in the north Caucasus except, as noted earlier, in some upland regions of Dagestan. Bajocian deposits overlie those below with erosional and, in places, angular unconformity [3, 9]. However, in contrast to the late Toarcian to early Aalenian regressive episode, the regression at the Aalenian-Bajocian boundary did not result in significant redistribution of sedimentary material. This is because the late Aalenian transgression had caused fluvial deltas, especially those in the northeast part of the basin, to migrate ~100 km to the North, so that sedimentation occurred at this time over a wide area of the Scythian plate. As a result, sedimentary material was not concentrated on the shelf edge, so that subsequent lowering of sea level did not cause its reworking and redistribution in more deeply marine parts of the basin. Sediment redistribution seems only to have occurred in those cases where the location of one of the deltas led to a considerable mass of sediment accumulating on a comparatively narrow part of the shelf, near to its edge, so that it was unable to disperse over a wide area of extensive shelf.

Later, in the Bajocian, one more episode of lowered sea level can be distinguished, although not apparently of great importance. It occurred at the boundary between the early and late Bajocian (Kumukhsk and Tsudakharsk Formations). It is situated at a sedimentary break which is recognized both in the east of the region and in the western Caucasus [3, 9, 10].

Marine deposits younger than early Bathonian are not known from the northern Caucasus. Judging from the occurrences of continental sediments in a few places, the sea had retreated far to the south at this time. Not until the Callovian did a new widespread transgression take place, marking the beginning of a new phase of development of the Caucasus.

Thus, it is possible to distinguish the following episodes of retreat of the sea in the Caucasus basin, apparently related to falling sea level: at the close of the early Pliens-

In fact, sedimentation in the Caucasus basin was dominated by the accumulation of thick sediment bodies in the shallowest waters. A relatively minor sea level drop (of a few tens of meters) was therefore in some places able to stop sedimentation, which sometimes resulted in a disconformity. For example, there were areas of shelf sedimentation during Domersk time in the Digoro-Osetinsk SFB, and at the end of the Toarcian within the Labino-Malkinsk SFB. In both of these cases the sedimentary succession was identical, from clay-siltstones to sandy sediments. As a result of the decreasing water depth in the basin in these areas with the eustatic lowering of sea level, brecciated and condensed beds of oxidized iron ore, or horizons with traces of subaerial weathering, are present. Where bodies of sediment had accumulated in coastal areas, such as in deltaic zones, the lowering of sea level caused these deposits to be reworked and redeposited in deep water.

Thus, it may be noted that the transgressive development of the Lower and Middle Jurassic basin was controlled on the whole by tectonic factors (downwarping of the basin floor), and by a generally prolonged eustatic rise in sea level. Regressive episodes were, apparently, caused primarily by relatively short-lived eustatic falls in sea level. Decreasing water depths led to a rapid retreat of the coastline, and even quite small eustatic movements of sea level resulted in sedimentation rates in the Great Caucasus geosynclinal flexure which were considerable. Local tectonic movements did not alter the general pattern of development of sedimentation, although they added to the complexity of the structure of sediment bodies.

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FINE-GRAINED TEPHROGENIC AND SEDIMENTARY ROCKS FROM THE AXIAL
ZONE OF THE VARISCIDES OF SOUTHERN MONGOLIA

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UDC 552.313.8:552.75(517)

Diagnostics of fine-grained rocks from volcanogenic-sedimentary complexes of the axial zone of the Variscides of Southern Mongolia are considered in this article. Two groups of rocks are distinguished: tephrogenic and sedimentary. It is established that the postsedimentational transformation of pyroclastics of various compositions led to the formation of various clay minerals. Two series of sedimentary formations are recognized: jasper and phtanite; argillites, siliceous argillites, clay silicites, and silicites are distinguished as the silicic-bearing rocks in each series. The admixture of tephra in these rocks is established from the high values of the anorthite-albite component.

Diagnostics of fine-grained rocks cause the greatest difficulty in volcanogenic-sedimentary complexes of eugeosynclinal basins of the past. To a significant degree this is caused by the migration of fine volcanogenic, terrigenous, and hydrogenic components into the sedimentation. Various types of fine-grained rocks take part in the structure of the volcanogenic-sedimentary complexes from the axial zone of the Variscides of Southern Mongolia, which were studied in detail in the Gurvan-Saikhan and Dzolen ranges. The indicated ranges are in the territory of the northern half of the Zaaltaisk Silurian-Devonian paleobasin, in the limits of which three zones are distinguished. These zones are distinguished by the type and character of their vulcanism, which is on the whole defined by the specifics of volcanogenic-sedimentary accumulations in these territories. From south to north (from the axis of the basin to its periphery) the following complexes formed: terrigenous-tuff-lava (Khadatulinsk), terrigenous-lava-tuff (Berkheulinsk), and lava-tuff-terrigenous (Gurvansaikhansk).

VOLCANOGENIC-SEDIMENTARY COMPLEXES

Lithological analysis of proximal (in relation to zones of vulcanite extrusion) sections of all complexes reveals not only points of similarity, but also their specifics. They are united by a two-level structure: lavas dominate in lower sections, while in the upper sections tephra prevail for a general homodromic trend of vulcanism in the entire Zaaltaisk basin. It is entirely regular that an increase of the explosivity of vulcanism was accompanied by growth in the quantity of volcanoterrigenous clastics, because the explosions on the one hand supplied juvenile material to the sedimentation basin, and on the other hand they contributed to the destruction of the volcanic structures, which led to the formation of a large mass of detrital intra-basinal material, whose quantity sharply grew through time. Both volcanic (lava and tephra), and volcanoterrigenous material form the base of all volcanogenic-sedimentary complexes.

Volcanic activity in the three cited zones of the paleobasin was distinct. This is reflected in the degree of differentiation of the volcanic series, the petrographic-petrochemical features of the vulcanites, and the types of eruptions [1, 2].

The terrigenous-tuff-lava (Khadatulinsk) complex, which formed in the axial part of the Zaaltaisk basin, is represented by lavas from basalts to andesite-dacites, with predetermination of porphyritic varieties, containing interlayers and lenses of tuffs, tuffopelites, jaspers, and volcanoterrigenous sandstones and siltstones. The lava sequence essentially alternates with a detrital sequence (400-500 m), in which volcanoterrigenous rocks and tuffs of intermediate and acid composition prevail. They contain polymict sand-

Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 16-27, March-April, 1989. Original article submitted December 29, 1987.

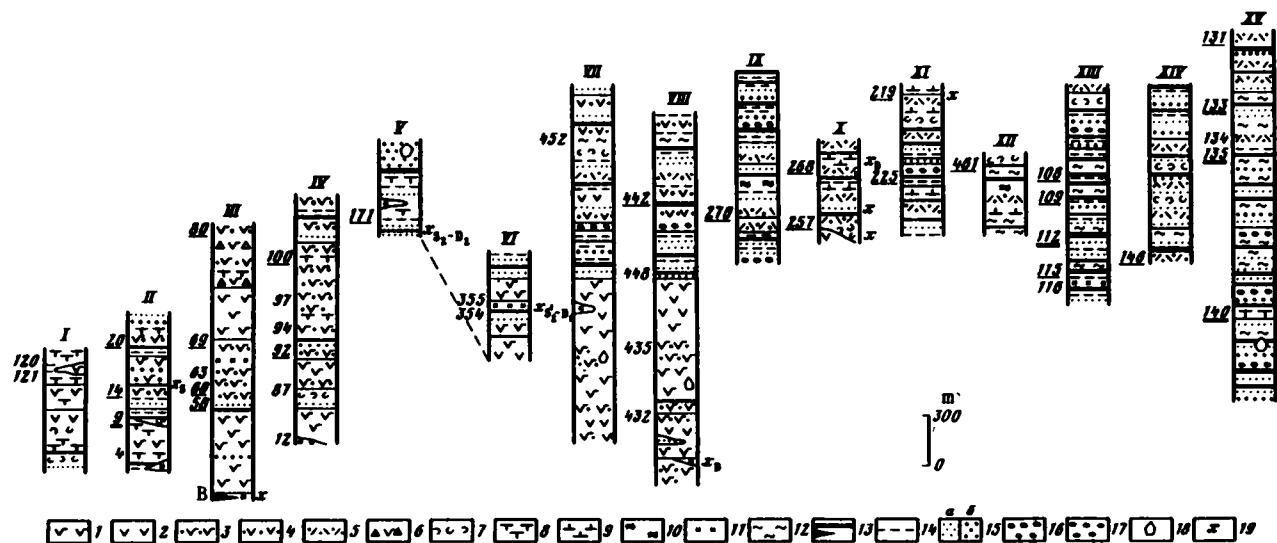


Fig. 1. Sections of the Berkheulinsk and Gurvansaikhansk complexes of the Zaaltaisk zone of Mongolia: 1) basalts; 2) andesites; 3-5) tuffs (3) basic; 4) intermediate; 5) acid; 6) basic tuff-breccia; 7) tephroids; 8) tuffopelites and pelitomorphous tuffites; 9) siliceous tuffites; 10) tuffosilicites; 11) jaspers and jasper-like rocks; 12) phtanitoids; 13) argillites; 14) siltstones; 15) sandstones [a) fine and medium grained; b) medium and coarse grained]; 16) gravelites; 17) conglomerates; 18) olistoliths; 19) places of radiolaria concentration, for determined varieties with indicated ages. The numbers on the column's left are the numbers of the samples analyzed by chemical (nonunderlined), x-ray structural (underlined with one line), and both (underlined with two lines) methods. I-XV are the sections of the complexes [I-V) Berkheulinsk, VI-XV) Gurvansaikhansk]. Section locations: I-V) Gurvansaikhansk range [I) northern slope of Mount Bayan-Tsagan; II) east of Mount Khara-Tologoi; III) north of Baga-Khavigain spring; IV) southwest of Mount Berkhe; V) west of Khabtsgaityn-Gol valley]; VI-X) Dzolen range [VI) south of Ubtu well; VII, VIII) western termination of the Dzolen range, 7 km between sections; IX, X) southwest and northwest of Tal well]; XI-XV) Gurban-Saikhans range (XI) south of Duvén-zhiin-Khundii creek valley; XII) Khorkhoityn-Kholoi natural boundary; XIII) north of section IV; XIV) northeast of Mount Galcharyn-Shuvun; XV) northwest of Mount Nomgon.

TABLE 1. Sedimentary Types of Fine-Grained Rocks from the Zaaltaisk Zone of Mongolia

Complex	Tuffs	Tephrogenic rocks	Tuffites	Sedimentary rocks	
				clay	siliceous
Khadatulinsk	Sedimentary, intermediate Acid	Tuffopelites -	- Siliceous	Argillites	
Berkheulinsk	Basic	"	Pelitomorph ic	"	"
Gurvansaikhansk	Basic, intermediate Acid	"	" Siliceous (tuffo-silicites)	"	Jaspers, Phtanitoids

stones, siliceous tuffites, lenslike bodies (up to 20 m) of plagioporphyrries, andesitic porphyrites, and single interlayers (<1 m) of dark grey argillites.

Accumulation of the terrigenous-lava-tuff (Berkheulinsk) complex occurred to the north of the Khadatulinsk complex. This is predominantly made up of aphyric pillow basalts and andesite-basalts with subordinate flows of andesites containing lenses of hyaloclastic breccias and hyaloclastites; clay jaspers with radiolaria are developed in the interpillow spaces of the lava flows. As in the preceding complex, the volcanites are built onto a detrital sequence, but are of significantly different composition. There is much hyaloclastic and basic volcanoterrigenous material in it, to which tephroids, tuffopelites, tuffites, argillites, and jaspers are subordinate. In more distal sections of the complex (relative to the zones of basaltoid alteration) the quantity of the lava component is decreased, volcanoterrigenous rocks, tephroids, tuffites, tuffopelites, and argillites become most representative; mixtitic horizons are locally developed (Fig. 1).

Zones of extension, recorded by proximal deposits of the two complexes characterized above, were compensated to the north of the Zaaltaisk basin. A subduction zone arises almost synchronously with them, and within its limits an island arc lava-tuff-terrigenous complex (Gurvansaikhansk) is formed [6]. It is formed by a wide spectrum of lava accumulations from basalts to dacites, both aphyric, and prophyric. As a rule, the flows are divided by thick (several tens of meters) packets of tuffs, tephroids, volcanoterrigenous rocks and jaspers. Above the tuffo-lava accumulations lies a thick (1000 m and greater) tuffo-terrigenous sequence, built up by volcanoterrigenous and polymict sandstones, siltstones with subordinate silty pelites, gravelites, seldom conglomerates; horizons of intermediate and acid tuffs are characteristic; in addition, tuffites, phtanitoids, jaspers, and mixtites occur.

In the recent structure of the Gurvan-Saikhhan and Dzolen ranges deposits of the Gurvan-saikhansk complex are most developed, particularly its upper tuffo-terrigenous part, the Berkheulinsk sequences are less dispersed and outcrops of the Khadatulinsk accumulations are extremely limited. They are generally sheared and metamorphosed, and by virtue of this neither chemical, nor x-ray structural analysis of the fine-grained rocks of this complex was performed.

A complex approach was utilized for the diagnostics of the fine-grained rocks of the Berkheulinsk and Gurvansaikhansk complexes. Its basis was lithologic-facies and volcanologic analyses of surrounding sequences [1]. Discrimination of individual types of fine-grained rocks was carried out, taking account of their detailed petrographic study, data of chemical analyses with conversion into mineral composition by the method proposed by Khvorova et al. [9], and x-ray analysis of the phase composition of clay fractions. Diffractograms were plotted on the DRON-1 diffractometer with CuK_α radiation at an intensity of 35 kV and current strength at 20 mA. The well-known manuals of Brindley [11], Brown [12], Drits et al. [4], and Gradusov [3] were utilized for the identification of the clay minerals. Quantitative estimates are given by Biscaye [10].

The primary types of fine-grained rocks developed in the volcanogenic-sedimentary complexes of the Zaaltaisk zone of Mongolia are presented in Table 1. Two groups are distinguished among them: "tephrogenic" and sedimentary. The term "tephrogenic" is arbitrary, since pyroclastic and volcanogenic-sedimentary (mixed) rocks are also considered here, but they form a discontinuous series, connected by a single source of volcanic material.

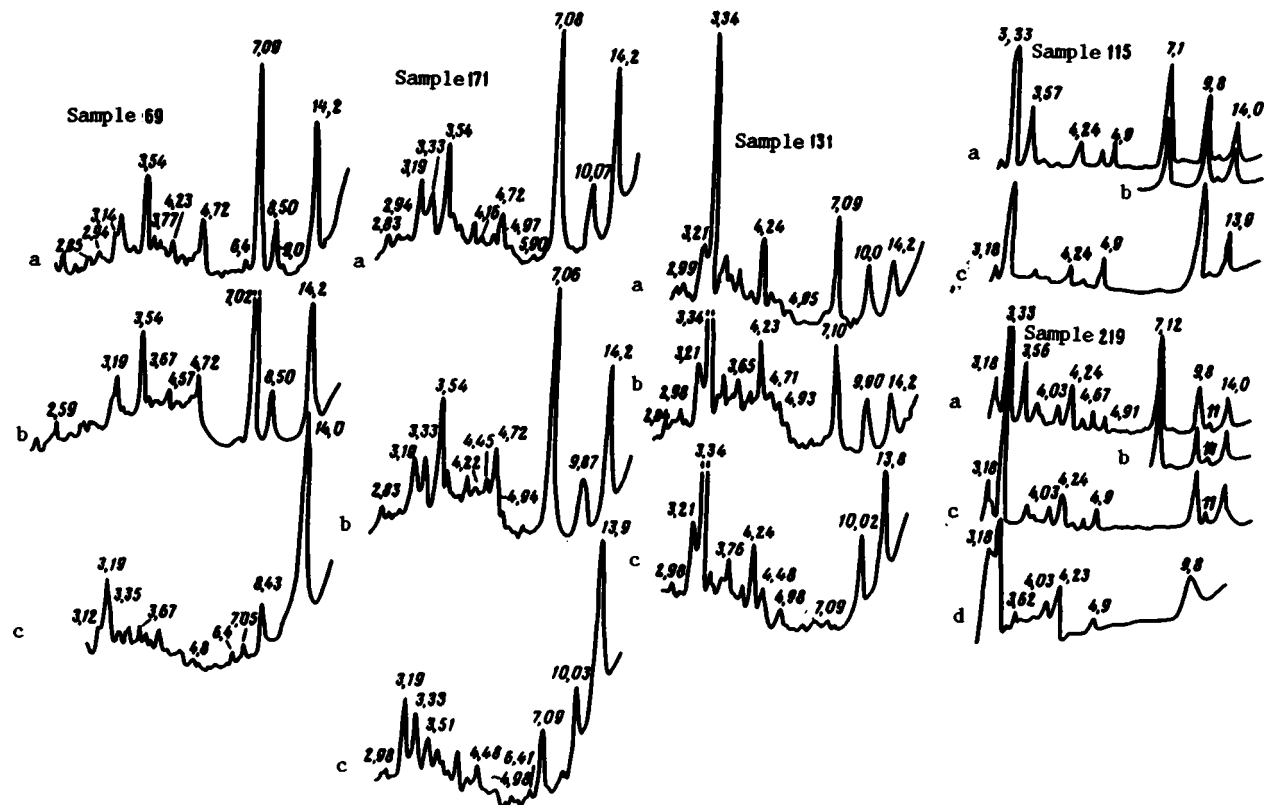


Fig. 2. Diffractograms of the fine-grained (<0.001 mm fraction) rocks of the Zaaltaisk zone of Mongolia. Sample 69) Hyaloclastite; sample 171) tuffopelite; sample 131) acid tuff; sample 115) argillite; sample 129) spongiol silty pelite. State of samples: a) natural; b) saturated with glycerine; c) fired at 550°C; d) processed with 10% HCl.

TABLE 2. Mineral Composition of the Clay Fraction (<0.001 mm) of Tephrogenic and Sedimentary Rocks from the Variscides of Southern Mongolia, %*

Rock group	Sample number	Rock type	Color	Clay minerals			Associated minerals			
				hydro-mica	chlorite	mixed layer	feld-spars	quartz	cris-tobal-lite	zeo-lites
Basaltic tephra and its derivatives	14	Finely detrital hyalotuff	Purple	—	80	—	10	5	5	—
	20	Same	"	—	85	—	10	—	5	—
	80	"	"	—	80	—	15	—	5	—
	58	Hyalotuff	Grey-green	—	80	—	10	—	Traces	10
	60	Finely detrital hyaloclastite	"	—	80	—	10	Traces	5	5
	69	Same	"	—	85	—	5	—	Traces	10
	92	Finely detrital hyaloclastite	"	—	85	—	10	—	5	—
	100	Tuffopelite	Green	—	85	—	10	—	5	—
Acid tephra and its derivatives	171	"	"	25	60	—	10	—	5	—
	140	Pelitomorphic tuffite	Grey	35	50	—	5	5	5	—
	146	Vitric tuff	Black	70	10	—	5	5	5	—
	131	Same	Green grey	50	35	—	5	10	—	—
	257	Crystallovitric tuff	"	55	20	5 (H-Ch)†	10-15	5-10	5-10	—
	270	Same	Black	70	15	—	5-10	5-10	—	—
	268	Siliceous tuffite	"	55	20	5 (H-Ch)	5-10	5-10	5-10	—
Sedimentary group	9	Jasper series argillite	Purple	70	15	—	10	—	5	—
	46	Phtanite series argillite	Black	35	50	—	10	—	5	—
	109	Same	"	35	45	—	10	5	5	—
	112	"	"	30	50	—	5-10	10-15	5	—
	108	"	Dark grey	50	25	5 (H-Ch)	5	10	5	—
	135	"	"	60	20	—	5	15	—	—
	219	"	"	60	25	3 (H-Ch)	5-10	10-20	—	—
	115	"	Grey-green	50	30	trace (H-Ch)	5-10	10-15	—	—
	225	"	"	65	15	5 (H-Ch)	5-10	10-20	—	—
	442	"	Black	60	20	trace (H-Ch)	5-10	5-10	5-10	—

*The percent content of minerals from the total of the clay fraction is presented.

†H-Ch: hydromica-chlorite phase.

TABLE 3. Content of Several Elements in Rocks of the Mongolian Zaaltaisk Zone

Component	Berkheulinsk complex				Gurvansaikhansk complex		
	basalt (6)	basaltic tuff (3)	tuffopelite (1)	tuffite (2)	andesite-basalt (3)	andesite-basaltic (2)	tuffite (1)
SiO ₂	49,47	49,48	50,69	52,46	53,54	55,10	59,76
TiO ₂	1,26	0,83	0,76	1,03	1,40	1,10	0,68
Al ₂ O ₃	15,26	15,04	14,83	15,67	17,01	15,38	17,26
Fe ₂ O ₃	6,49	6,10	8,28	4,25	6,26	6,39	2,30
FeO	7,03	7,00	2,91	3,59	2,70	3,11	3,02
MnO	0,2	0,21	0,40	0,19	0,08	0,20	0,17
MgO	4,13	5,44	1,83	3,32	2,71	3,00	2,24
CaO	7,28	7,23	6,47	9,99	4,64	3,90	2,71
Na ₂ O	3,74	3,63	4,12	2,43	6,29	6,01	2,65
K ₂ O	2,2	1,31	1,09	0,85	1,75	2,34	6,10
P ₂ O ₅	0,4	0,17	0,18	0,22	0,71	0,57	0,19
H ₂ O ⁺	2,10	2,65	1,50	2,31	1,89	1,90	2,19
H ₂ O ⁻	0,26	0,28	0,02	0,22	0,36	0,70	0,24
Cr	21	20	25	42	59	<10	24
Ni	25	23	19	26	50	≤15	17
V	256	287	185	136	185	137	97
Cu	126	147	86	80	142	132	52
Co	34	31	19	20	30	16	8
Zn	102	94	60	92	85	185	75
Sr	900	431	404	1878	651	682	485
Zr	128	74	140	167	190	210	254
Ba	492	210	200	90	400	415	969

Note. Analyses were completed in the chemical-analytical laboratory of the GIN Academy of Sciences of the USSR. The number of the analyzed sample is shown in brackets; the content of oxides is given in mass %, elements in g/ton, while Cr, Ni, V, Cu, and Co are determined by spectroscopic method, and Zn, Sr, Zr, and Ba by x ray.

TEPHROGENIC ROCKS

Variations in the composition and structures of the tuff are the most characteristic formations of this group for all of the volcanogenic-sedimentary complexes. Fine-grained tuffs are represented by vitric varieties, rarely by crystallovitric varieties, independent of composition.

Basaltic and andesite-basaltic tuffs (see Fig. 1, samples 14, 20, 58, 60, 63, 69, 80, 87, 92, 94, 97, 432, 435) are made up of two forms of glasses: chloritized and ferruginized; variations in the quantitative ratios of these two components determine the rock color, which varies from grey-green and green, through purple-green and green-purple to purple. Ferrous glasses are most represented in the Berkheulinsk complex. Ferrous oxide dominates in the green tuffs, ferric oxide dominates in the purple tuffs while the Fe₂O and FeO contents are commensurate in the intermediate colored varieties. X-ray structural analysis of tuffs (Fig. 2) showed that their clay fraction is completely formed by chlorite (Table 2); quartz, feldspar, sometimes zeolites and amphibole are diagnosed. These are characteristic minerals occupying fine fractures in tuffs. It is necessary to stress that feldspars occur in form of a crystalline phase of fine-grained tephra in the Gurvansaikhansk complex. Basic variations in the composition of the pyroclastic material are recognized on a chemical level the content of primary petrogenic and minor elements.

Geochemical features of the explosive material clearly stand out in comparison with the lava material [2], while they are distinct for the fore-arc type (Berkheulinsk) and island arc type (Gurvansaikhansk) vulcanism. In the Berkheulinsk tephra, the contents of almost every basic petrogenic and minor element drops, except magnesium, vanadium, and copper. The average values of such components as silicon, aluminum, iron, and manganese are commensurate in the tuffs and lavas (see Table 3). The average content of crystallization water in hyalotephra is 0.55 mass % greater than in lavas.

TABLE 4. Chemical and Mineral Composition of Clay-Siliceous Rocks of the Jasper Series, %

Components	Berkheulinsk complex			Gurvansaikhansk complex				
	B*	9	12	363	354	448	355	116
SiO ₂	63,98	66,71	86,75	69,64	70,75	74,78	89,67	92,41
TiO ₂	0,58	0,55	0,30	0,85	0,60	0,59	0,17	0,16
Al ₂ O ₃	13,55	13,83	5,29	9,58	11,84	10,69	3,01	0,23
Fe ₂ O ₃	6,80	5,42	2,86	7,97	4,72	3,16	1,79	2,10
FeO	0,92	1,28	0,67	1,22	0,65	1,15	0,69	None
MnO	0,12	0,09	0,01	0,07	0,04	0,17	0,07	2,92
MgO	1,00	1,07	0,61	1,46	1,61	1,43	0,89	None
CaO	1,53	1,68	1,09	2,03	2,13	1,55	1,12	1,05
Na ₂ O	5,07	2,39	0,34	2,82	2,18	4,66	0,34	0,10
K ₂ O	2,65	3,97	1,32	2,14	2,44	0,61	1,24	0,14
P ₂ O ₅	0,16	0,13	0,03	0,08	0,01	0,06	0,08	None
H ₂ O ⁺	0,66	2,17	0,48	1,27	2,23	0,50	0,55	0,03
H ₂ O ⁻	0,27	0,40	0,15	0,48	0,63	0,22	0,22	0,15
SiO ₂ (free)†	6,89	17,06	71,61	29,63	32,01	34,04	72,42	94,40
Chlorite	3,51	3,61	2,21	5,25	5,69	5,20	3,14	None
Anorthite	6,23	6,60	4,61	8,48	8,75	6,54	4,59	2,48
Albite	48,13	21,86	3,35	27,45	20,85	45,81	3,24	1,05
Hydromica	35,22	50,85	18,20	29,16	32,68	8,39	16,58	2,06

Note. Analyses were performed in the chemical-analytical laboratory of the GIN, Academy of Sciences of the USSR.

*Sample numbers (see Fig. 1) and rock types: B) Tuffo-argillite; 9) argillite; 12) clay jasper; 363-354) siliceous argillite; 448) siliceous tuffo-argillite; 355) clay jasper; 116) jasper.

†In this and the following table the mineral composition is recalculated from data of chemical analysis and normalized to 100%.

If the Berkheulinsk volcanic series is weakly differentiated and not distinguished by silicon oxides in its lava and tephroic accumulations, then in the Gurvansaikhansk continuously differentiated complex the tephra of one and the same differentiate are 1.5 mass % times more acid than lava. If there are more basalts among the lavas, then andesite-basaltic varieties predominate among the tuffs. The content of many petrogenic and minor elements drops in the explosive phase (see Table 3), chrome and nickel particularly sharply, and the quantity of Fe, Mg, K, and the lithophilic components Sr, Zr, Ba, as well as Zn increase; the average content of crystallization water remains at the same level as in the lavas (1.9 mass %).

Tuffopelites are found in close paragenetic connection with basic (and intermediate) tuffs (samples 100, 120, 171). These are green and green-grey rocks, represented by fine intergrowth of albite, chlorite, and epidote (sometimes prehnite), relatively enriched by sodium and calcium (see Table 3). If we convert these elements to albite and epidote by the method proposed by Khvorova et al. [9], then they come to 70% of the mineral composition of the rocks (albite >40% and epidote nearly 30%). If we conditionally carry out this calculation for tuffs associating with the tuffopelites, then the values are commensurate and vary from 65 to 75%. The same order is also established for purple varieties of tuffopelites, the mineral composition of which it is impossible to determine microscopically due to the wide development of iron hydroxides (Fe₂O₃ up to 8 mass % for FeO 3%). In terms of x-ray structure, the clay fraction of the tuffopelites is completely composed of chlorite: in individual cases a mica is diagnosed with 10-15% expanding interlayers, and its content reaches 15% in the <0.01 fraction, and 25% in the <0.001 mm fraction (see Fig. 2). The close connection with the tuffs and the identity of the secondary transformation indicate the principally tephroic nature of the tuffopelites, and the predominance of Na-Ca in the components makes it possible to relate them to albite varieties [9].

Yet another type of rock which may be defined as pelitomorphous tuffite is derivative of basic and intermediate pyroclastics (samples 4, 121, 140). This is a green and green-grey fine-grained formation. Its basic mass is either completely chloritized, or transformed into a chlorite-epidote or albite-chlorite-epidote aggregate. The sedimentary com-

TABLE 5. Chemical and Mineral Composition of Clay-Siliceous Rocks of the Phthanite Series, %

Components	Argillite			Phthanitoid
	112*	219	135	452
SiO ₂	61,37	61,79	64,04	83,30
TiO ₂	0,66	0,66	0,53	0,25
Al ₂ O ₃	16,15	16,32	15,82	7,42
Fe ₂ O ₃	2,15	1,91	1,82	1,08
FeO	4,46	4,43	2,76	1,44
MnO	0,15	0,14	0,08	0,14
MgO	1,56	2,06	1,38	0,49
CaO	3,43	2,06	2,36	1,21
Na ₂ O	2,81	2,82	1,16	2,60
K ₂ O	3,96	3,72	5,03	0,43
P ₂ O ₅	0,20	0,15	0,19	0,02
H ₂ O ⁺	2,37	2,71	2,63	1,22
H ₂ O ⁻	0,16	0,18	0,42	0,12
CO ₂	Absent	0,20	0,70	Absent
Corg	0,42	Absent	Absent	Absent
SiO ₂ (free)	6,31	10,05	14,16	60,59
Chlorite	5,19	7,08	4,50	1,82
Anorthite	13,27	8,22	8,94	5,24
Albite	25,30	26,21	10,23	26,24
Hydromica	49,91	48,41	62,14	6,07

Note. Analyses were performed in the chemical-analytical laboratory of the GIN, Academy of Sciences of the SSSR.

*Sample numbers (see Fig. 1).

ponent is generally represented by biogenic silicon-radiolaria, and feldspathic and quartzic silt and mica of the muscovite type sometimes occur. The free silicon content obtained by conversion of chemical analyses [9] does not exceed 10% of the mineral composition of the tuffites, while the Ba-Ca component varies (as in the tuffs) from 65 to 75%. They are essentially categorized as orthotuffites [5]. The quantity of hydromica varies from 6 to 18%. The high (6.1%) content of K₂O in a tuffite of the Gurvansaikhansk complex (see Table 3) is connected with the post-sedimentational introduction of calcium, which is concentrated in hydromica occupying fine fractures in the tuffite. Chlorite dominates in the <0.001 mm fraction, and the quantity of hydromica does not exceed 35%.

The characterized tephrogenic rocks, which are derivatives of basic and intermediate pyroclastics, arose either as a result of post-sedimentational transformation of tephra, or by its mixing with biogenic siliceous material for an insignificant contribution of fine terrigenous material.

Among acid tuffs correlated to the upper parts of the Khadatulinsk and Gurvansaikhansk complexes fine and fine-grained crystallovitric and vitric varieties (samples 131, 134, 146, 257, 270) are most widely developed; ash structure is locally preserved in them. This is often a fine intergrowth of quartz, albite, and chlorite; crystalloclastics of plagioclase and quartz are encountered. The clay fraction of tuffs is formed by chlorite and mica, containing on the order of 5-10% expanding interlayers; feldspar and a significant admixture of quartz are diagnosed (see Fig. 2). In the clay fraction of the Gurvansaikhansk acid tuffs, the contents of the hydromica component are rather high, and vary from 50 to 70% (see Table 2). This is caused by the potassium specialization of acid differentiates of island arc vulcanism. Low values for primary petrogenic components are characteristic (mass %): TiO₂ 0.37; Al₂O₃ 8.78; MgO 0.76; CaO 1.62; Na₂O 1.56; K₂O 1.83 for high content of SiO₂ (79.11). Conversion of the preliminary mineral composition of acid tuff leads to the following, %: free SiO₂ 50, hydromica 25, albite 15, anorthite 7, and chlorite 3. The microelement content is lower than Clarkian, for inclusions (g/ton): Cu 56, Co 10, Zn 68.

Acid tuffites are genetically connected with acid pyroclastics (samples 268): green and bluish-grey fine-grained rocks, made up of a devitrified chlorite-quartz-albite vitric component (sometimes containing relicts of ash structure), in which radiolaria and rarely siliceous spicules of sponges and plant detritus are dispersed, as well as flakes of the muscovite type of hydromica (up to 65%) and chlorite (up to 30%), and in the form of admix-

ture layer hydromica-chlorite (hi-ch) mineral is present. Interlayers (a few tens of centimeters) rarely occur of green-grey and pink tuffosilicites composed principally of quartz in intergrowth with albite and a small quantity of chlorite. Pink varieties are impregnated by iron hydroxides. Recrystallized radiolaria are encountered. The presence of albite and chlorite in the siliceous mass, and of inseparable post-sedimentational minerals of acid tuffs, attest to the contamination of acid glass in silicites.

SEDIMENTARY ROCKS

It is possible to subdivide the fine-grained sedimentary formations into two subgroups: jasper and phtanite, each of which combines clay, clay-siliceous, and siliceous rocks connected with the paragenetic and geochemical commonality.

Rocks of the jasper series are developed in all three complexes, and are mostly represented in their lower lava parts. They also occur in the intermediate tuffs and terrigenous accumulations in the form of thin interlayers. They are characterized by a red or purplish color gamma, determined by high iron oxide contents (Table 4); FeO values vary from 0 to 1.22 mass %. The quantity of free silicon is defining for clay-siliceous rocks. The following rock types are distinguished by this parameter, %: argillite 1-25, siliceous argillite 25-50, clay jasper* 50-90, jasper >90.

X-ray structural analysis of the clay fraction in the argillites showed that it is made up of hydromica (up to 70%) and chlorite (up to 15%); feldspar and quartz are diagnosed from the accompanying minerals. For conversion of the argillite chemical analyses to mineral composition with defined contents of free silicon, albite, anorthite, chlorite, and hydromica [9] in the argillite (see Table 3, sample 9), it is established that hydromicas are nearly 50% and chlorite more than 3% of the total mineral composition of the rocks.

In siliceous varieties (samples 363, 354), its quantity is reduced to 30% mainly due to an increase in free silicon, often represented by radiolaria. Mineral varieties are distinguished among clay rocks which are defined as tuffoargillites (sample B, 448) which are characterized by high values of albite component. The tuffoargillites are horizontally layered, caused by their interlayer enrichment by silt-fine sand acid tephra, represented by opaline quartz, and plagioclase; chloritized fragments occur. Pyroxenes, serpentinites, and limestone detritus of bryozoans and crinoids are encountered locally.

Jaspers are primarily represented by clay varieties (samples, 12, 355), nonradiolarian and radiolarian, the primary components of which are silicon and hydromica. An admixture of acid tephra is locally observed in them (quartz, plagioclase, chloritized fragments) and in such cases the rock may be defined as a clay tuffojasper. Jaspers with content of (free) SiO_2 > 90% seldom occur. Denser siliceous rocks are generally strongly fractured and recrystallized. As a rule, the fractures are filled by fine-grained quartz aggregate. Later generation fractures filled by ore material are observed in some jaspers (see Table 4, sample 116); the iron-manganese-titanic modulus of such jasper, constituent 39 in Strakhov's data [7], attests to the presence of exhalative material in the rock. Ferric and phosphoric oxides are not diagnosed in the jasper; carbon dioxide reaches a total only of 0.40%, and carbon of 0.11%; high (1200 g/ton) values of strontium (RFA) are characteristic. Apparently, not only iron and manganese, but also carbon (hydrocarbon) and strontium are of an exhalative origin. Such divergence from the norm is not recorded in any other analyzed rock types from the jasper series; their iron-manganese-titanic modulus varies from 9 to 18.

Rocks of the phtanitic series are connected with the upper part of the Gurvansaikhansk complex of tuffoterrigenous formations. Their formation occurred in a back-arc basin. This is a series of dark-grey and black argillites and phtanitoids, in which ferric oxide dominates over ferrous oxide (Table 5). In comparison with the rocks of the jasper series, they display higher values of aluminum, potassium, phosphorus, and organic material (if it is present). For argillites with high content of anorthite-albite components (samples 112, 219), increased concentrations of some minor elements are characteristics, g/ton: Cu 70-93, Ba 1100-1600. It is possible these argillites contain an admixture of pyroclastic material.

Pure varieties of argillites seldom occur. They generally have an admixture of silty material; quartz, feldspars, organic detritus, sometimes radiolaria. The clay fraction (see

*Khvorova [8] cuts the content of (free) SiO_2 off at 75%, subdividing these silicites into strongly clay and clay.

Fig. 2) is composed from hydromica and chlorite, the quantitative proportions of which vary from 35 to 65% (see Table 2). A small quantity (no more than 5%) of an interlayered hydromica-chlorite phase is seldom noted. This is often concentrated in fine fractures filled by green-yellow interfering material.

Phtanitoids are dark grey and black cryptocrystalline and fine-grained quartz rocks, impregnated by microcrystals of pyrite, generally containing fine silt of quartz and plagioclase, and single radiolaria. It is necessary to define black silicites with high values of anorthite-albite components (see Table 5, sample 452) as tuffophtanitoids, which are characterized by increased concentrations of Cu and Ba, up to 1.5 times their Clarke values in the sedimentary cover of the earth.

Black argillites are most represented and associated both with intermediate and acid tuffs, tephroids, and tuffites, and with intermediate-acid volcanoterrigenous rocks. Phtanitoids are insignificantly developed and generally form layers from 10 to 20 cm and rarely 50 cm in thickness. They are grouped in packets up to 1.5-3 m in thickness and they participate in the structure of packets (15-30 m), which are principally made up of fine platy black silty pelites and argillites.

Lithologic-facies analysis of the volcanogenic-sedimentary complexes of southern Mongolia [1] showed that the terrigenous detrital accumulations that developed in them are intrabasinal and arose mainly as a result of the destruction of volcanic structures, which formed in the Zaaltaisk basin. Clays, paragenetically connected with volcanoterrigenous clastics, are also derivatives of the disintegration of basic, intermediate, and acid volcanic rocks. Siliceous material forms the hydrogenic component, the derivations of which were siliceous organisms, primarily radiolaria. Mixing in sedimentation of fine pyroclastic, volcanoterrigenous and hydrogenic material led to the formation of the large gamma of the mixed rocks.

Analysis of fine-grained rocks from the axial zone of the southern Mongolian Variscides showed that during their formation they underwent strong alteration, particularly in the stage of epigenesis-categenesis, when the primary mass of their clay minerals was formed. At the same time, post-sedimentational transformation of juvenile volcanic material of varied petrochemical composition led to the formation of varied clay minerals: chlorite evolved from basic glasses, hydromica and chlorite in roughly equal quantities or with predominance of the hydromica component evolved from an acid differentiate with potassic specialization of island arc vulcanism (the Gurvansaikhansk complex). Analogously, the composition of the tephra (basic or acid) determines the mineralogy of the clay fraction (principally chlorite or hydromica) and in mixed fine-grained rocks pertaining to orthotuffites.

There are two series among the clay-siliceous rocks in paragenesis and geochemical relationship: jasper and phtanitoids; the components of their formation in free silicon acid (obtained by conversion of chemical analyses) are subdivided into argillites, siliceous argillites, clay silicites, and silicites. Their clay fraction is also represented by hydromica and chlorite, whose ratios vary strongly from sample to sample; an interlayered hydromica-chlorite component is sometimes diagnosed; and probably has a superimposed character in a series of cases. The admixture of tephroic material in sedimentary fine-grained rocks is established by the high values of anorthite-albite components.

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VERY SHALLOW WATER DEPOSITIONAL COMPLEXES IN THE RIPHEAN OF THE SOUTHERN URAL MOUNTAINS

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UDC 552.5:552.72(470.5)

Very shallow water (nearshore-continental, littoral, bay-lagoonal, and sublittoral) sedimentary complexes of a stratotypic Riphean section in the Bashkir Megaanticlinorium are discussed. Information on the distribution of shallow water complexes in the Riphean sections and their interrelationship with other lithofacies complexes led to reconstruction of the general characteristics of early, middle, and late Riphean depositional basins in the western slope area of the Ural Mountains. The cited examples of genetic histories are similar to those of Riphean formations of the Siberian Platform and its marginal zones, Scotland, Norway, and China.

Reconstruction of the principles that govern various sedimentary processes, of the evolution of sediment- and rock-accumulating basins, and formation conditions of associated mineral resources [30] are the main objectives of contemporary lithological studies. One of the most pressing tasks is the understanding of depositional basin evolution during earth history. Regional and global reconstructions of this type do exist for extensive time intervals in earth history (Paleozoic, Mesozoic-Cenozoic). At the same time, the Precambrian sedimentary complexes that represent very long periods have been insufficiently studied.

Areas with Riphean sections in the periphery of the Siberian and East European Platforms are singular areas for the understanding of the basic principles that govern the evolution of sediment- and lithogenesis and comparative analysis of sedimentary complexes of various upper Precambrian sedimentary basins. A distinct pattern of alternation of sediment associations, different in composition and genesis, takes place in these areas. In the past the Siberian and Ural region Riphean deposits had been unevenly studied. A sufficiently detailed lithofacies map and numerous summaries [1, 4, 7, 10, 19, 20, 22] are available for Siberia but publications that deal with the stratotypic Riphean section and the formation conditions of the complexes and their evolution, are still scarce. Assumptions on the sediment-forming processes and evolution of the sedimentary basins, as in the 1940s and 50s, are based on broad geological summaries. In this context the detailed study of the Riphean sedimentary complexes of the southern Urals is important. Reconstruction of their paleogeographic formation conditions and establishment of a conceptual foundation for the formation analysis of "ancient" complexes with regard to sediment formation is needed. It would result in

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the formulation of a sedimentation process model, covering approximately one billion years and huge expanses of the East European Platform and Ural area.

The present paper deals with characteristics of very shallow (littoral, bay, and lagoonal) Riphean sediment complexes of the Bashkir Megaanticlinorium. These sediments are regarded as the nearshore marine facies of the shelf superzone [9].

In agreement with Yu. P. Kazanskii's classification, beach, low-tidal flat and lagoonal subzones have also been identified. Reineck and Singh [28] characterized the modern nearshore terrigenous detrital deposition zones and identified shore, intertidal and coastal lagoon facies. Sand predominates in the shore zone. The upper foreshore ranges from the eolian dunes to mean tide level. Lamination is mostly horizontal in the sands, sometimes with layers with indications of current ripples. Density separation during storms leads to heavy mineral concentrates on the upper foreshore. The lower beach zone or tidal flat-zone occurs seaward.* Muds, silts, clays, fine sands, and other sediments are deposited here, in zones approximately parallel with the shoreline. The width of the intertidal flat zone usually is several hundred meters, sometimes a few tens of kilometers. Nalivkin [18] cited the nearshore Jutland watt zone as an example. The zone there is 20-25 km wide, with a total area of 440 km². The sediment distribution in most intertidal-shallow subtidal facies conforms to a regular pattern [23] and primarily depends on the current and wave regimes [8]. The finest sediments are deposited at the highest tide level. Silty-sandy and sandy deposits form seaward. Alternating currents with varying directions and velocities resulted in thin alternating sand, aleurolite and mud layers. A third element of the nearshore zone is the presence of shallow, shore-parallel lagoons. These basins became separated from the open sea and now are connected to it through only a narrow pass. Mostly silty and muddy sediments accumulate in modern lagoons. These occur in areas of limited sand deposition. Lagoonal sediment deposition patterns are quite variable and complex. The settings also include barrier islands (shoals), ebb-tidal deltas, deep tidal channels, erosional tidal cuts, swamps and lakes, salt marshes, sounds, etc. [23].

It has been held for long [8] that tidal deposits (tidalities) only occur in the intertidal zone. In the past few years it was shown that shallow subtidal deposits play a major role in the world ocean. Therefore, these should also be present in large quantities in the geologic sections. The problem of tidalite deposit identification also arises. Schopf [34] discussed this in the greatest detail. A detailed analysis of the diagnostic features of ancient tidal complexes was given by Klein [43, 44], Ginsburg [39], et al. A major role in the identification of intertidal deposits is played by periodic reversals in the directions and velocities of tidal currents. Such deposits include various interlayered lithogenetic rock types, with indications of intraformational erosion, reactivation surfaces, alternating sandy (traction-saltation transport) and fine-grained muds (suspension transport) with flaser bedding, the interlayering of thin-bedded sandstones of varying dip directions with aleurolites and clays, as well as the close intertwining of subaerial and subaqueous sediments.

Reineck and Singh [23] have shown that none of the bedding types are exclusively diagnostic of intertidal deposits and noted vectorial bimodality of cross-stratification as a diagnostic tool for tidalite recognition, as well as such surface sediment structures that indicate periodic desiccation and subaerial exposure of the sediments.

Due to development of principles that govern sedimentary basins, interest in Precambrian sedimentary complexes has increased in the past few years [29]. A summary of data on the early Precambrian [31, 32] has shown the generally shallow water character of these sedimentary basins. According to Timofeev and Kholodov, paleogeographic reconstruction of various Proterozoic periods in the Baltic Shield, Kazakhstan, North America and Australia generally indicates the presence of very shallow epicontinental marine basins in these areas. Despite the general tendency toward increased contrasts in the relief of the earth surface, during the Riphean the character of sedimentary basins did not significantly change during the Riphean and the majority are characterized by small water depths and widespread island chains, shoals, banks, underwater rises, etc.

The shallowest (littoral and similar) facies have been described from practically all of the Precambrian. In the following, we are going to review some of these.

*The lower beach zone is absent along tideless seas and the upper beach zone gradually merges with the prefrontal zone [23].

Early Precambrian (~3 billion years) intertidal deposits provided very interesting examples [26, 37]. The Pongola Subgroup, northern Natal, contains orthoquartzitic sandstones with tin siltstones and argillite layers of shallow marine origin. They include sandstone and alternating sandstone-clayey shale beds with structures that are indicative of very shallow water origins. Reactivation surfaces, ripples and feathery cross-bedding occur in sandstones. In interlayered units, the tidal origin is indicated also by desiccation cracks, breccias of shale fragments, interference ripples, and double-crested ripple ridges. Clayey shales occur occasionally that apparently formed on upper tidal flats. Tidal and nearshore marine deposits that accumulated in estuarine-deltaic settings in front and behind barriers, have also been described from the upper part of the Swaziland Subgroup (~3.3 billion years) [38].

Detailed lithofacies studies of the Lower Proterozoic deposits of the Udokansk Series indicated distribution of various facies in the sections and their role in the formation of copper mineralization [14, 28, etc.]. The Udokansk Series is represented by sediments of three complete sedimentary cycles, developed during recurrence of similar paleogeographic conditions and formation of similar sedimentary facies types. The very shallow water sandy-aleurolitic sediments of lagoonal-bay zones and diagnostic features of periodic desiccation are typical of sections of the Ayansk, Aleksandrovsk, Butunsk and Naminginsk Formations. In the Udokansk Series the horizon is characterized by one of the ore-bearing intervals [28]. Semiisolated, very shallow water conditions were most favorable for the formation of this type of sedimentary complex during the middle and final evolution stages of the sedimentation cycles. Layered sandy-clayey and silty-clayey deposits also occur. They form in zones, similar to modern clay-silt playas (takirs) and were associated with sediments of lagoonal facies; finely layered aleurolites with numerous desiccation cracks [11].

Klein [42] described tidal facies from the "lower fine-grained quartzite" section in the middle interval of the Dalradian Group of Scotland with four lithologic rock categories: massive, fine-grained quartzites, lenticular-layered quartzitic aleurolites, finely layered argillites and dolomites. The studied textural-structural rock characteristics led Klein to recognize two facies. Facies 1 consists of massive or cross-stratified orthoquartzites, sometimes with asymmetrical ripples. The middle and upper beds have trough- and tabular plane-parallel bimodal-bipolar sets of cross stratification. Facies 2 includes aleurolites and argillites with thin orthoquartzite layers. These are characterized by numerous desiccation fractures, thin horizontal and fine lenticular layering and ripples. These Middle Dalradian facies represent an upward-fining sequence. The sediment structure analysis, the position of the facies in the sections, their mutual interrelationships and comparison with modern tidal sediments suggested that the deposits formed predominantly in tidal settings. Sandstones of Facies 1 were regarded as having formed in subtidal or low-inter-tidal facies while Facies 2 was deposited on the upper tidal flats.

The Upper Precambrian Vadsö Group in Finnmark, northern Norway, includes a complex sequence of alluvial and marine sedimentary rocks with widespread tidal deposits. The Veidnesbof Formation, basal unit of the Vadsö Group, was subdivided into Facies A, B, and C [40]. Facies A contained subarkosic red sandstones with fine, interlayered channel deposits, considered sediments of bifurcating stream channels. Facies B included cross-stratified shallow marine orthoquartzites. The upper part of the Veidnesbof Formation the orthoquartzites alternated with tidal deposits of Facies C. Rhythmic alternation of aleurolites and argillites, cross-stratified and flaser bedding and desiccation cracks were the most typical sediment structures in these deposits. A number of ripple types occurred on the bedding surfaces: one with flat ridge tops, another with two parallel ridge sets, interference ripples with superimposed small perpendicular ridges, and other sedimentary structures. Intraformational conglomerates with sandstone and argillite fragments also occurred, deposited in small channels, similar to modern tidal river channel deposits.

Tidal deposits are known from the Upper Precambrian section in China. More than thirty types of shallow water sedimentary structures have been described from the Ming Tombs District Lower Proterozoic-Riphean carbonate rocks (~1977-884 million years) [47]. Along with coarse pebbly sandstones of alluvial origin with trough-cross bedding of various dimensions and slump structures, units with alternating, light gray sandstones and dark gray silty argillites also occur. These are characterized by numerous structures of shallow water origin. Flaser and lenticular bedding, ripples, desiccation and syneresis cracks, intraformational conglomerates caused by erosion, raindrop imprints and wave splash marks indicate formation in tidal, occasionally dry settings. Fine-grained, well-sorted quartz sandstones with lin-

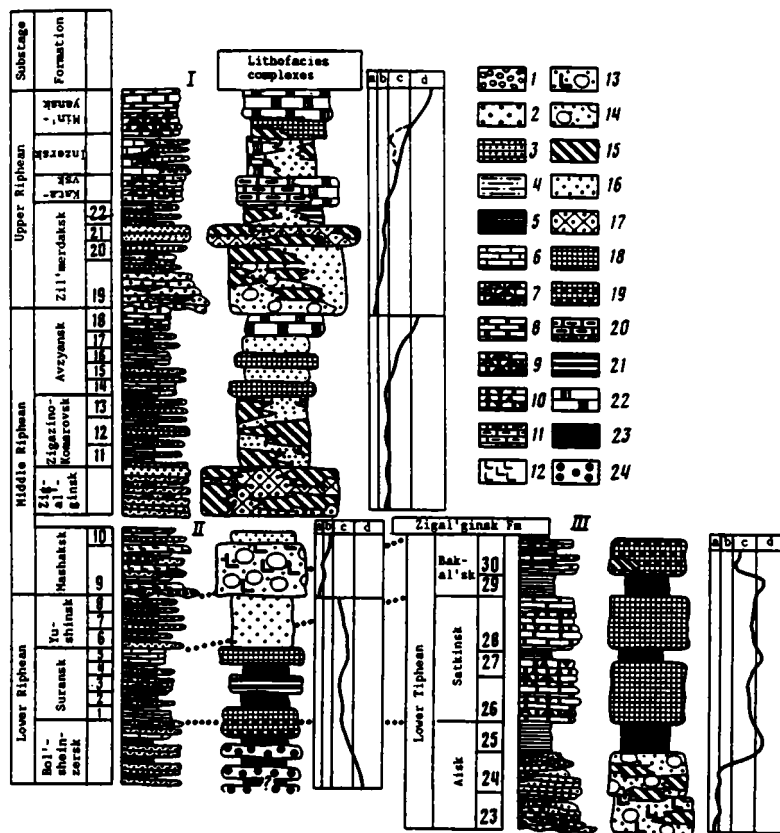


Fig. 1. Main horizons of very shallow water (terrigenous and carbonate) sediment complexes in stratotypic Riphean sections of the southern Ural: 1) conglomerates and gritstones; 2) coarse- and medium-grained sandstones; 3) fine-grained sandstones; 4) aleurolites; 5) clayey shales and argillites; 6) limestones; 7) stromatolitic limestones; 8) dolomites; 9) stromatolitic dolomites; 10) dolomites with layers of breccia, composed of flat fragments; 11) clayey limestones and marls; 12) acidic and basic volcanic rocks; 13-24) lithofacies complexes; 13) volcanosedimentary, mostly continental deposits; 14) conglomeratic-aleurolitic-sandy deposits of alluvial and alluvial-deltaic origin; 15) very shallow water terrigenous and carbonate deposits; 16) sandy-aleurolitic and sandy-aleurolitic-clayey beds of shallow marine origin; 17) sands of high quartz content and sandy-aleurolitic deposits of shallow and nearshore marine origin; 18) shallow marine carbonate deposits; 19) alternating beds of shallow marine terrigenous and carbonate deposits; 20) clayey-carbonate; 21) fine-grained terrigenous deposits of marine origin; 22) marine carbonate formations; 23) fine-grained, terrigenous carbonaceous of mostly marine origin; 24) terrigenous deep water deposits - deposits of gravity flow; I) type stratigraphic column of Middle and Upper Riphean deposits of the western limb of the Bashkir Meganticlinorium; II, III) stratigraphic columns of Lower Riphean deposits of the central and the northeastern regions of the megaanticlinorium, respectively. Members: 1) Min'yaksk; 2) Berdagulovsk; 3) Angastaksk; 4) Serdausk; 5) Lapyshinsk; 6) Vyazovsk; 7) Bagaryshinsk; 8) Sukhinsk; 9) Kuz'elginsk-Karansk part of the Mashaksk Fm; 10) Shakitarsk and Yamantau; 11) Sereginsk; 12) Ambarsk; 13) Tukansk; 14) Kataskinsk; 15) Maloinzersk; 16) Ushakovsk; 17) Kutkursk; 18) Revetsk; 19) Bir'yansk; 20) Nugushsk; 21) Lemezinsk; 22) Bederyshinsk; 23) Navyshsk; 24) Lipovsk and Udinsk; 25) Kisegansk and Sungursk; 26) Lower and Upper Kusinsk; 27) Polovinkinsk; 28) Lower and Upper Satkinsk; 29) Makarovsk; 30) Upper Bakal'sk. Deposit types: a) continental; b) very shallow water; c) shallow water; d) marine.

goid ripples, interlayered within these units, indicate littoral and barrier island facies. Diagonal cross stratification, interference ripple sets with double crests, flaser and lenticular bedding, desiccation cracks, slump microfolds, syneresis structures, erosional surfaces with intraclasts and various stromatolite types occur in the carbonate rocks, mostly marls and dolostones. Feathery cross stratification is common in carbonate rocks with intraclasts. The clearly expressed sedimentary structures throughout the ~4500 m total thickness of the sequence indicate that accumulation occurred mostly in tidal settings. Sediments of supra-, inter-, and subtidal zones were distinguished.

The very shallow Riphean nearshore marine deposits are presently known in many areas of the Siberian Platform and its folded margins.

Tidal deposits, wett tidal flat depositional complexes and nearshore marine zones were described from the NW slope of the Anabar Massif in Lower Riphean sections of the Mukunsk and Ust'-Il'insk Formations [5]. Nearshore littoral formations were represented by units of interlaminated argillites and aleurolites. Small asymmetrical current and wave ripples, fine cross lamination and hieroglyphs (sole marks) and, on the lower bedding plane surfaces, desiccation cracks have been observed in the aleurolites. L. P. Belyakov thought that deposits of the Ust'-Il'insk Formation formed in very shallow water facies, where even the term shoreline could only be conditionally used.

In the Turkhansk region, sandy-aleurolitic-argillitic sediments of the Middle Riphean Strel'nogorsk (Bezymensk) Formation were composed of nearshore marine deposits that occasionally dried out. According to Mirosnikov [17], various ripple types, desiccation fractures, various hieroglyphs (sole marks), gradational-, wave-, trough-, and lenticular bedding types were typical. Lithological-geochemical rock characteristics indicate that during Strel'nogorsk time these sediments formed in a shallow basin of decreasing salinity [3].

Very shallow water, nearshore marine deposits are characteristic of the Sosnovsk, Potoskuisk, Pogoryuisk, Shuntarsk, and Tokminsk Formations of the Yenissei Ridge Riphean [6, 24, 25].

Very shallow, nearshore marine deposits are known from many Riphean intervals in the Uchur-Maisk area of SE Siberia. They are best displayed in the Lower Riphean Omakhtinsk Formation [26, 27] that consists of fine, rhythmic alternation of sandstones, aleurolites, and argillites, with numerous structures that indicate periodic desiccation in sandy, oncogenic, and stromatolithic dolomites. The basal portions of the rhythms are characterized by halite crystals, desiccation cracks and ripples. The carbonate rocks of the middle portion of the rhythms are without sedimentary structures that would indicate subaerial drying, but they are characterized by various cross stratification types and widespread small-scale unconformity and erosional surfaces. Lateral alteration features in the Omakhtinsk Formation section are also of interest. Stromatolite-bearing and chemical deposits pinch out almost completely in the direction of the Aldan Shield and are replaced by sandy and oncogenic dolomites and in sections, located farthest west, by purely terrigenous deposits [27].

The stratotypic sections of the southern Ural contain very shallow water littoral-continental and nearshore marine deposits in the Lower Riphean Aisk and Bakal'sk Formation [2, 12, 13], the Middle Riphean Zigal'ginsk, Zigazin-Komarovsk and Zvzyansk Formations [21] and Upper Riphean Zil'merdaksk and Inzersk Formations [15]. Such deposits thus are known in practically all terrigenous (author means: detrital siliciclastic) and a number of carbonate horizons (Fig. 1).

Our lithofacies studies during the past few years indicated that the wide range of sediments that formed under recurring dry conditions may be subdivided into three major subgroups. The first includes those units that were closely associated with the alluvial-deltaic complex. The second group consist of sandy, and sandy-aleurolitic deposits that formed in open and partly isolated littoral areas with deeply indented shoreline patterns and in periodically dry bays and lagoons; the third includes sublittoral sediment of high- and very high-energy nearshore, shallow marine zones.

Nearshore-continental deposits occur in Riphean sections of the Bashkir Meganticlinorium. Mostly fine-grained sandstones, aleurolites and argillites occur with fine cross lamination, wavy cross stratification and wavy stratification, with desiccation fractures, closely associated with the alluvial-deltaic complex.

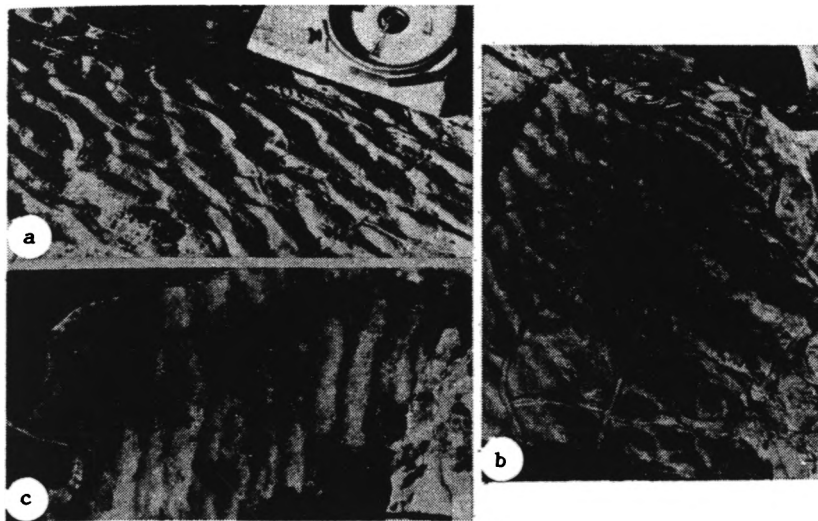


Fig. 2. Sedimentary structures of littoral zone sandy sediment facies (Lemezinsk Member, Zil'merdaksk Formation). a) Asymmetrical, crescent-shaped ripples on bedding surface of fine-grained sandstone, with superimposed desiccation cracks; b) large, symmetrical sinusoidal wave ripple, with a set of small interference ripple ridges and superimposed desiccation cracks; c) symmetrical, straight, slightly bifurcating wave ripples with steep ridges, on bedding surfaces of medium-grained sandstone.

Sandy-aleurolitic-clayey sediments in continental-coastal planes. These are located in the Bir'yansk Member of the Upper Riphean Zil'merdaksk Formation. The sediments range from a few to 40 m thick. Characteristically, irregularly alternating sandstones (10-15 cm), aleurolites (2-7 cm) and shales (3-7 cm) occur here. Numerous desiccation cracks, well-developed wavy layering and cross-stratification, formed by migrating ripples are typical on the upper sandstone and aleurolite bedding surfaces. Occasionally, small protrusions occur on the bedding planes, resembling partially dissolved halite crystals. The rocks are greenish-gray, gray or reddish-brown.

Interlayered fine-grained sandstones may occur in the same facies within the Lower Riphean Aisk Formation. Lenticular beds and carinate sandstone bodies are also interstratified with them. The aleurolites typically consist of 2-3 cm thick units with horizontal lamination and fine lenticular cross stratification. Occasionally they also include thin layers of sandy matter with quartz grains of maximum 2 mm diameter. Desiccation cracks and molds often occur on the lower bedding planes of sandstones and aleurolites. Perpendicular to the bedding plane, a peculiar wormy structure developed through deformation that resulted from pressure, exerted by desiccation cracks. Occasionally, carinate protrusion occurs as the result of the erosion of underlying clayey-aleurolitic beds and the subsequent filling of minute hollows by sandy matter. These interlaminated beds are 5-7 m thick.

The interrelationship of this facies with sediments of dominantly continental, alluvial-deltaic origins leads one to assume that they formed on continental-coastal plains that periodically were inundated, to turn dry again later. Takir playas provide a contemporary analog.

Terrigenous-carbonate facies of continental coastal planes include two sediment types. Massive or thin-bedded, gray and dark-gray dolomites with significant terrigenous admixture represent the first. Thin, horizontal, fine bedding, broken in individual layers and minor units, the layer is characterized by alternation of beds with different composition. The dolomite bedding surface was uneven, hummocky, with occasional wave ripples. The second type includes limestones and sandy limestones with medium-to-small-scale inclined, mutually intersecting cross lamination, large ripples and knobby bedding plane surfaces. The limited distribution of this sediment facies in the Bur'yansk Member of the Zil'merdaksk Formation where they occur as thin lenses among terrigenous littoral-continental deposits with discernible admixture of terrigenous matter, indicate that they accumulated in small basins, possibly in ephemeral lakes of the coastal plain.

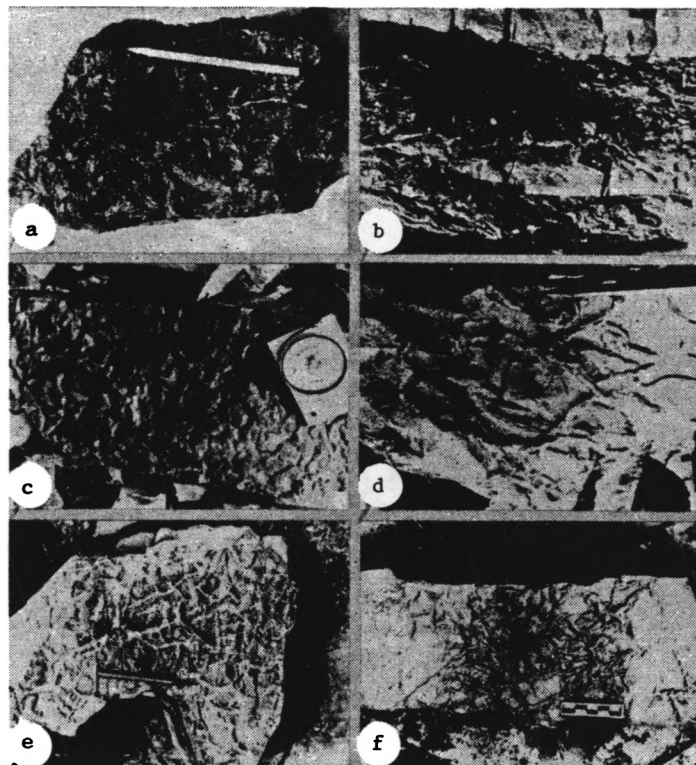


Fig. 3. Sedimentary structures of sandy-silty rocks. These sediments periodically were wetted and dried in a coastal plain setting and in a strongly dissected coastal zone. a, c) Impressions and molds of desiccation cracks on bedding planes of carbonaceous aleurolites from a sequence of alternating aleurolites and argillites with disturbed layering; b) general bedding features of similar unit; d-f) molds with irregularly shaped desiccation cracks on siltstone- and fine grained sandstone bedding planes. Zigazin-Komarovsk Formation (a-c), Bedershinsk Member of Zil'merdaksk Formation (d-f).

The next large very shallow sediment complex in the Riphean sections of the Bashkir Meganticline is represented by sediments of open and semi-enclosed coastal waters with strongly indented shorelines and lagoonal-bay sediments of periodically dry basin areas. These formed in high- or low-energy conditions, respectively, in parts of shallow waters basins that periodically became inundated, later to turn again into dry land.

Sand beach deposits typically occur in the Upper Riphean (Bir'yansk Member, Zil'merdaksk Formation) and, less frequently, in the Lower Riphean Aisk Formation. These are mostly fine-grained, well sorted sandstones, with typical low-angle cross stratification, uni- or multidirectional, mutually intersecting layering or horizontal lamination. The laminae are outlined by Ti-magnetite and ilmenite-concentrates. These ore-bearing sandstone units are 15-25 m thick.

Littoral facies of sandy deposits are most typical of two horizons: the Middle Riphean Zigal'ginsk Formation and the Lemezinsk Member of the Upper Riphean Zil'merdaksk Formation [15]. Sediments of this facies are characterized by fine- and medium-grained, gray or yellowish gray sandstones. Numerous flakes of chocolate-colored or light-green clayey shales formed through disintegration of thin clay layers during desiccation crack development. In a number of instances slightly deformed, simple, isolated flaser laminae occurred in the sandstones, reflecting wavy or wavy cross lamination. Molds and various desiccation cracks occurred on the lower bedding planes of sandstones, while various-sized ripples, orientation bedforms occurred on the upper bedding planes, often with superimposed desiccation cracks (Fig. 2). The deposits formed in occasionally dry areas, while the psammitic sediments reflect the high level of littoral (wave) energy. The presence of flaser bedding, presently most widespread in sublittoral and intertidal zones [23] was important. The remarkable

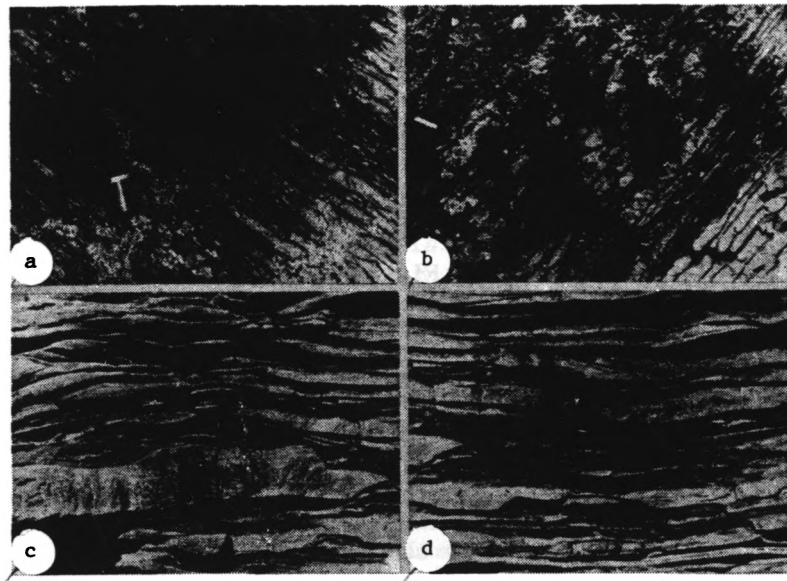


Fig. 4. Layering features in alternating sequence of siltstones and fine-grained sandstones. They are part of the sandy-silty, high energy, shallow nearshore facies. a, b) Ripple cross-laminated, lenticular, and lenticular cross-laminated, with elements of flaser bedding; c, d) ripple-laminated and lenticular cross-stratification, with alternating and varying dip directions in the lenses. Inzersk Formation.

variety of bedding plane-sedimentary structures here is also typical of sand deposits in present watt facies [8]. The sandy littoral zone deposits were 4 to 25-30 m thick or thicker.

Carbonate sediments of the open littoral zone in the Upper Riphean Min'yarsk Formation were represented by dark gray or almost black, pelitic-finely crystalline limestones with thin horizontal, very fine horizontal, wavy-cross lamination, lenticular cross lamination, and flaser bedding. Molds of desiccation cracks occurred on the lower bedding planes of the limestones. The sediments formed in very shallow parts of the basin, exposed to periodic desiccation. Sediments accumulated on banks, flat-topped shoals and islands that extended slightly above sea level. The deposits are interconnected with clayey-limey, and limey sediments of shallow and open basin areas. They are 5-7 to 50-80 m thick.

Sandy-aleurolitic-clayey sediments of periodically dry/flooded areas: continental coastal plain and strongly dissected nearshore areas. The facies are most typical of the Upper Riphean (Bederyshinsk and Bir'yansk Members of the Zil'merdaksk Formation) and Middle Riphean (Zigazin-Komarovsk Formation) (Fig. 3). The Zil'merdaksk Horizon consists of inter-layered red, 2-5 to 7-10 cm thick sandstone beds, aleurolites (3-7 cm thick) and argillites or clayey shales (5-15 to 60-80 cm thick). The sandstones and aleurolites contain wavy and wavy-cross lamination. Low-angle cross sets, ripple drift lamination and flaser bedding have been observed. The bedding surfaces display numerous current ripples, wave ripples with superimposed desiccation cracks. In a number of sections of the Beder'shinsk Member the bedding surfaces of red silty argillites displayed pseudomorphous replacements after halite crystals. Sediment thickness of this Upper Riphean facies ranged between 10-100 m. The sediments are closely interrelated with shallow and nearshore marine deposits.

Units of relatively thin, irregularly alternating, dark gray, almost black, fine-grained, carbonaceous-clayey, layered or massive or indistinctly fine-layered aleurolites and light gray coarse aleurolites occur in the described facies of the Zigazin-Komarovsk Formation. Various types of bedding occur in the coarse aleurolites; thin horizontal, inclined wavy-cross lamination, low-angle cross lamination. About 10-15% of the thin (2-3 cm) layers in these beds represent sharply outlined ripples. Simple and complex flaser bedding occurs in a number of instances. The coarse aleurolite beds, more than 3-4 cm thick, are characterized by complex combinations of various types of layering. Ripple drift, wavy-

cross and flaser bedding and ripple lenses occur. The dip orientations of laminae in the ripples are uni- and multidirectional. Clearly expressed desiccation cracks occur on the upper bedding surfaces of the aleurolites. These fissures terminate in the unit and do not reach the underlying coarse aleurolite beds. The distance between adjacent desiccation crack horizons was 80 cm. The sediments of this facies were 40-50 m thick or thicker. Typically, they were associated with shallow marine, sandy-aleurolitic-clayey sediments, enriched in organic matter (OM).

The composition and lithological-geochemical data [16] indicate that the sediments accumulated in a humid climate during the Middle Riphean, while under near-arid conditions in the Late Riphean.

Sediments of similar genetic conditions have been described by Krupenin [12] among sediments of the upper part of the Lower Riphean Bakal'sk Formation. These units were represented by argillites, aleurolites, and sandstones, a few tens of meters thick and characterized by widespread lenticular and cross-bedded sedimentary structures, small-scale erosional features, desiccation cracks and ripples. The sandstones occasionally are dominantly massively bedded. In sections of the Upper Bakal'sk Member, these formations were associated with sandy-aleurolitic sediments of the marine wave zone, sandy deposits of marine currents, and nearshore aleurolitic-clayey sediments of coastal basins.

The third group of very shallow water sediments in the Upper Riphean section of the Bashkir Meganticlinorium formed in sublittoral, high energy, and very high energy zones and consist of two facies:

Sandy-aleurolitic sediments of nearshore high energy shallow marine basins include Upper Riphean interlayered, fine-grained sandstones, fine- and coarse-grained aleurolites with lenticular cross-, wavy-, and subhorizontal lamination or relatively uniform sandstone and coarse aleurolite layers with lenticular cross stratification and wavy layering (Fig. 4). Interlayered sandstone beds are 2-15 cm thick; their bedding surfaces are covered with small interference, asymmetrical, and symmetrical ripples. The lower bedding surfaces have sole marks that resemble molds of current jets or primary current lineations. Layering in the lower and middle parts of most sandy beds is poorly expressed and characterized by indistinct banding. The upper beds have inclined cross lamination. The aleurolitic beds are 1-15 cm thick. They are characterized by alternating dark and light colored lenses with clearly displayed fine cross- and wavy lamination. The dip orientations of the layers are uni- or multidirectional. Numerous lenses with uni- and multidirectional orientation of inclined small-scale cross-stratified units occur in the relatively uniform sandstone or aleurolite units of this facies. The lenses are outlined by color differences. On the bedding surfaces the lenses appear as asymmetrical current ripples. Section of the Upper Riphean Inzersk Formation include sediments of this facies, in association with sandy-aleurolitic deposits of zones of low energy shallow marine deposits. They are 40-400 m thick.

Sediments of this facies apparently formed in the shallow marine, high energy zone with combined surging currents of varying directions. This is indicated by varying lamina orientation in the sandy or aleurolitic lenses. A modern analog may be provided by sandy-aleurolitic-muddy, shallow, sublittoral North Sea sediment zones; these are characterized by very widespread development of lenticular cross-stratification [37].

Shallow, High-Energy Sandy Marine Facies. The Lemezinsk Member of the Upper Riphean Zil'merdak'sk Formation contains these deposits. In the westernmost section of the Lemezinsk Member these sediments are represented by medium-, occasionally fine-grained, relatively well sorted sandstones with medium and small scale, multidirectional cross-stratification, by ripples and desiccation cracks. Mutually truncating sets of herringbone cross-lamination occur. From 20° at the top, the dip angles decrease to 12-15° at the bottom of the series. the trough-sets are straight or of wavy outline. The cross-laminae often include small milk-white quartz pebbles. Deposits in this Upper Riphean facies were 10-30 m thick. The sediments are closely associated with littoral deposits of moderate energy shallow waters.

Sections of the Zigal'ginsk deposits of this facies contained fine- and coarse-grained, light gray or yellowish gray, thick-laminated sandstones. They included small and medium scale trough or inclined wedge cross-stratification, mostly with varying dip directions. the trough outlines are straight or slightly curved. The cross-sets are 1-3 mm thick, the dip orientation of vertically adjacent sets uni- or multidirectional.

The relatively coarse rock composition, the cross-stratification of complex types, and indications of subaerial sediment exposure suggest deposition in very shallow, nearshore, high energy settings, on surfaces of underwater accumulative bedforms that often emerged above water level.

Reconstruction of facies conditions of the Riphean Bashkir Meganticlinorium provides a fairly reliable picture of the original landscape and a model of the Riphean depositional basin on the western slope of the present southern Ural region. The available data lead to a number of conclusions.

The very shallow water deposits in the Riphean section of the Bashkir Meganticlinorium include three somewhat different sediment complexes. The first is a nearshore-continental complex, closely interrelated in the section with alluvial and alluvial deltaic sediments. These sediments are found in thin units and in general, against the background of continental deposits, appear ephemeral. The complex represents a period with contrasting paleogeographical features, including the source areas and the basins of final deposition [15].

The second category of very shallow deposits include the sublittoral sandy-aleurolitic sediments that formed under the influence of tidal currents [15]. They are most typical in a number of the Upper Riphean Inzersk Horizon sections. Based on modern analogs, the sediments suggest the presence of cratonic margins that had been converted into peneplains.

The third complex includes sandy-aleurolitic and aleurolitic sediments of bays, lagoons, and littoral zone. They have similar sedimentological characteristics at different stratigraphic levels. Their composition indicates humid or near-arid depositional conditions. During their deposition, the depositional basins formed a complex mosaic of environments; periodically dry and continuously wet conditions. Shallow marine sediments of the Zigazin-Komarovsk Horizon laterally and in the vertical sections are intricately interwoven with lagoonal-bay complexes. The paleogeographic composition of the Beredyshinsk Horizon (that corresponds to a similar member of the Zil'merdaksk Formation) indicate the adjacent position and complex intertwined nature of open marine zones, regions of shallow marine sedimentation, and extensive areas of very shallow water deposition [15]. Shoreline indicators and unquestionable continental deposits were absent in all studied sections. This shows the presence of flat-floored depositional basins, with variable locations and areal distribution. They included shoals and periodically dry areas, surrounded by low, intensively leveled nearshore-continental coastal plain landscapes. Despite differences in sediment source patterns and energy (hydrodynamic) conditions, the depositional basins had very similar aspects during Zigal'ginsk and Lemezinsk times. In a number of instances such conditions also characterized the times of carbonate deposition.

Analysis of information on the lateral and vertical distribution of Riphean sections of the very shallow Bashkir Meganticlinorium area deposits, along with data on the evolution of other sediment complex types allow us to assume that the sedimentary processes to some extent differed between the early, middle, and late Riphean times of sediment accumulation. Sedimentation occurred mostly in a passive continental margin zone.

This was clearly shown in the early Riphean Mayatnikov-type northeastern regions in the shifts from continental (rift-type) sedimentary and volcanic-sedimentary complexes to nearshore marine and marine (mostly carbonate) facies, and again to shallow marine (periodically lagoonal) conditions. The very minor role of Riphean very shallow water deposits is interesting. The cause probably was the limited size of the depositional basin; at certain times it was close to being a trough-type basin. The widespread distribution of thick Lower Riphean carboniferous terrigenous deposits of marine genesis is very important in this respect.

The middle Riphean depositional basin was characterized by indistinct transgressional histories. The general area was restructured geologically at the boundary between the early and middle Riphean. Rift-type volcanic and volcanic-sedimentary complexes (Mashak Formation) accumulated during the early stages of its existence and during early Riphean. While the sedimentary basin significantly expanded during the following long period, very shallow and shallow marine, sandy, and sandy-aleurolitic-clayey deposits accumulated under a humid climate. Apparently, the transgression during Zigal'ginsk and Zigazin-Komarovsk times lapped over a strongly dissected low coastal plain and involved shore zones of the basin, parts of which occasionally dried out, parts remained submerged. Shallow marine conditions proper persisted only at the end of the middle Riphean in the basin.

The late Riphean sedimentary basin developed differently. The marine basin contracted at the beginning of the late Riphean. Continental and nearshore deposits formed on the western flank of the basin, due to the erosion of granite-gneiss and meta-sedimentary rocks that had formed the basement of the Russian Platform. Although typical of the early and middle Riphean, the rift stage did not extend into the late Riphean. The sedimentary complex has an essentially different aspect at this time. Both the terrigenous and the carbonate deposits were mostly variegated. During the late Riphean carboniferous sediments were not typical in the subject area. A shallow marine, quartz-glaucopitic complex was established for the first time (Inzersk Horizon). Chemogenic marine carbonates accumulated during the middle and final stages of the late Riphean basin development. This fact underlines the essentially transgressive character of basin evolution. The appearance of a "regular" marine basin in late Riphean times apparently led to the widespread distribution of sublittoral stromatolites in the carbonate beds. The late Riphean marine depositional basin was larger than the earlier ones and included a large area in the present Ural region and the eastern zone of the Russian Plate.

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DOLOMITIC ROCKS OF THE BELORUSSIAN REEF AND THEIR GENESIS

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UDC 552.543:552.72(475)

On the basis of geochemical and mineralogical investigations of the dolomitic rocks of the Pinsk and Lapichsk Suites of Belorussia, we demonstrate the primary-sedimentary origin of the dolomitic components of these suites. Conclusions are drawn concerning the age-diversity of the deposits of the Pinsk and Lapichsk Suites (the first belongs to the middle reef, the second to the upper suite) on the basis of features associated with the distribution of heavy detrital minerals, manganese, and carbon isotopes.

The reef deposits of Belorussia have a total thickness of up to 1000 m. There is a sharp predominance of clastic, predominately sandy and silty-sandy rocks occurring over the major portion of its territory. Deposits of the lower (Bobruiskaya and Sherovichskaya series), middle (Belorusskaya series), and upper (Lapichsk Suite) reefs can be distinguished [13, 14]. They fill the Volyno-Orshanskii Paleotrough, a large, elongated structure of northeasterly strike. The lower reef formations occur within small, spatially disconnected areas coinciding with ancient negative, predominately grabenlike structures. Deposits belonging to the upper reef occur over a comparatively small (10-15 thousand km²) area in the central portion of the Volyno-Orshansk Paleotrough.

Dolomites and mixed dolomite-clastic (terrigenous) rocks have a subordinate significance in the Belorussian reef. They coincide with the Pinsk Suite of the middle reef and the Lapichsk Suite of the upper reef (Fig. 1).

The Pinsk Suite has a thickness of 460 m and is composed predominately of red oligo- and meso-mictic, fine-grained, often silty sandstones and coarse-grained siltstones with subordinate layers (from fractions of a meter to 2-5 m) of silty-clayey rocks. The latter impart an irregularly rhythmic structure to the stratum of the Pinsk Suite. The cement of the sandstones and siltstones is clayey, in places dolomitic. In the southern and central regions, the content of dolomite in the clastic rocks of the suite increases, and interlayers of sandy, more rarely almost pure dolomites, appear. The dolomitic and dolomite-containing rocks coincide primarily with boundaries of rhythms within which diverse indications of shoaling of the sedimentary basin are noticeable, along with frequent interruptions in sediment accumulation: dessication cracks, kaolinization, fissuring, and other hypergene alterations of rocks in the roofs of the rhythms; scouring and redeposition (in the form of fragments) of rocks from the roof of overlying rhythms subadjacent to the basal horizons. At the tops of the rhythms, the dolomitic rocks are usually red with an admixture of clastogenic sandy-silty and clayey material interlayered with sandstones, clayey siltstones, and clays. The rocks at the bottom of the rhythms are usually light- or rose-grey, with an admixture of coarse sandy material and fragments of the underlying rocks, including dolomitic varieties. Such rocks frequently grade into peculiar intraformational conglomer-

Institute of Geochemistry and Geophysics, Academy of Sciences of the Belorussian Soviet Socialist Republic, Minsk. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 43-57, March-April, 1989. Original article submitted July 15, 1988.

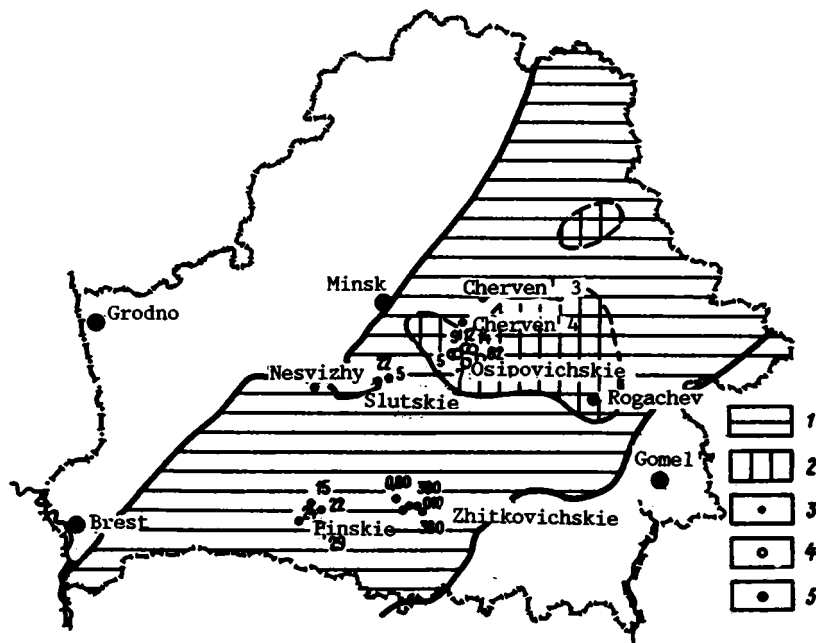


Fig. 1. Modern distribution of deposits of the Pinsk and Lapichsk Suites of the reef: 1-2) areas of occurrence of deposits of the Pinsk and Lapichsk Suites, respectively; 3-5) sections of boreholes in which dolomitic rocks were studied [3) Pinsk Suite, 4) Lapichsk, 5) Pinsk and Lapichsk Suites].

ates consisting of fragments and semiassimilated fragments of clayey siltstones, and other material cemented by dolomite with various admixtures sandy-silty material.

The dolomitic component of the rocks is intermediate- to fine-grained; in the clayey varieties, the dolomitic component is fine-grained to microgranular. The texture of comparatively pure dolomites is homogeneous massive. In sandy dolomites and dolomites enriched with coarse-clastic material, the dolomitic component is banded-mottled, bunched, brecciated, foliated, sometimes stylolitic joints (Fig. 2). The carbonate fraction of these rocks, according to the data of chemical and x-ray structural analysis, is represented by normal or nearly normal dolomite. Among the other carbonate minerals, one can find authigenic micro- and very fine-grained ferridolomitic (nodule-type concretions), siderite (pseudospherulitic aggregates), and secondary calcite (in vesicles and fissures).

The Lapichsk Suite is represented by a stratum with a thickness of up to 82 m. It is composed of irregularly interstratified oligomictic sandstones of diverse structure and degree of sorting with clayey-dolomitic or dolomitic cement, clayey and sandy siltstones, and dolomites of diverse structure and texture, frequently with an admixture of clastogenic material, and syngenetic dolomitic breccias. Layers of polymictic conglomerate, conglomerobreccias, and interlayers of clay are present. The clastic rocks are predominately red. Layers of grey sandstone enriched with finely dispersed carbonaceous matter are present.

The dolomites in the Lapichsk Suite form interlayers and beds with thicknesses of several centimeters to 3 m. A great diversity of coloration, structure, and texture are characteristic of these rocks. Two basic types of dolomites can be distinguished: chemogenic and organogenic (phytolithic). Also a number of transitional varieties occur: chemogenic-organogenic, organogenic-brecciated, syngenetic dolomitic breccias. The rocks are red (brownish-, red-brown, brownish-rose, sometimes with lilac tinting) and of variegated color due to an alteration of bands and spots in the reddish-brown range and lighter tones (roses and yellow-greys).

The chemogenic dolomites are massive and layered. Vesicular (with films of iron oxides and manganese), ferruginous, and partially silicified varieties are present. The degree of crystallinity in the dolomites is inhomogeneous: there is an alteration of interlayers and areas from pelitomorph to coarse-grained in structure (Fig. 3). A still greater struc-

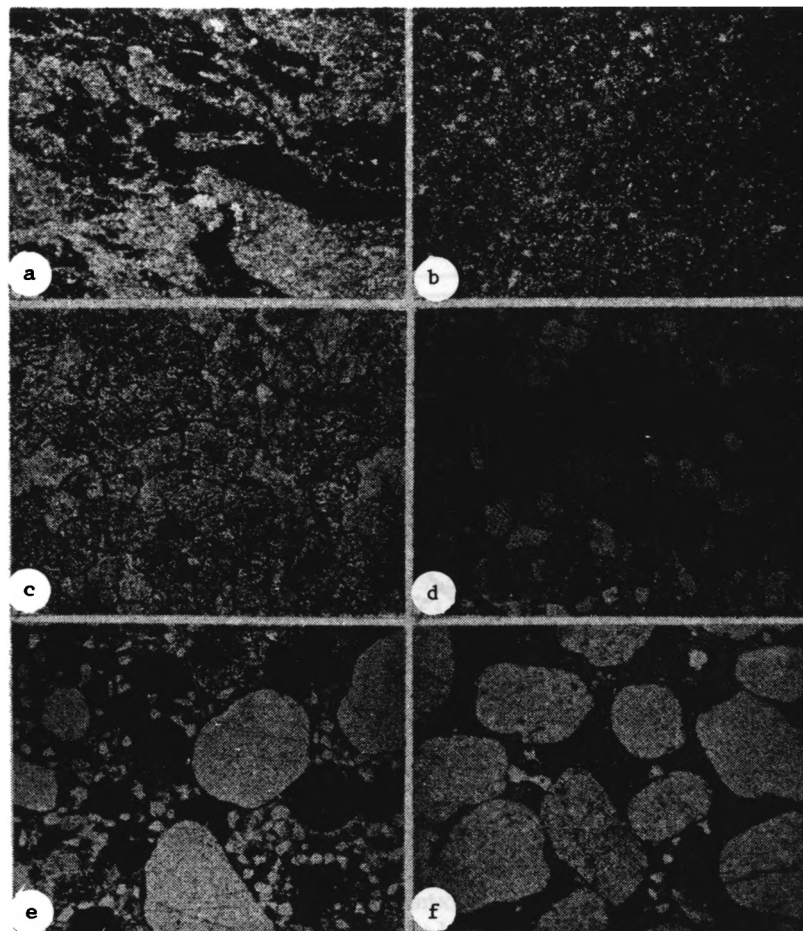


Fig. 2. Microphotographs of rocks of the Pinsk Suite: a) micro- and very fine-grained dolomite with fragments (dark) of syngenetic ferruginous hydromicaceous clay (drillhole Cherven' 4, depth of 465.0 m, 40 $\times$); b) micro- and very fine-grained dolomite (drillhole Cherven' 3, depth of 405.0 m, 80 $\times$); c) intermediate-grained dolomite (drillhole Cherven' 3, depth of 405.0 m, 80 $\times$); d) siltstone with basal dolomitic cement (drillhole Cherven' 3, depth of 325.0 m, 80 $\times$); e) fine-grained sandstone with basal dolomitic cement; dark) rounded fragments of fine-grained dolomite (drillhole Cherven' 4, depth of 455.0 m, 40 $\times$); f) sandstone, intermediate-grained with basal very fine- and fine-grained dolomitic cement (drillhole Osipovich-7, depth of 687.0 m, 40 $\times$).

tural and textural variegation is characteristic of organogenic dolomites. This is due to a repeated alteration of phytolith structures with oncolites, catagraphs, and areas of recrystallization located within them, and a leaching of carbonate and reworked clayey material, iron oxides, and manganese (see Fig. 3b, d, and e). The dolomitic breccias are predominantly composed of unrounded fragments of dolomites (massive, schistose, vesicular-porous, phytolith) dolomitic sandstones and sandy-silty rocks. The cement of the breccias is dolomitic with various admixtures of clastogenic material. Chemical and x-ray structural studies of the dolomites and dolomitic rocks of the Lapichsk Suite indicate that the carbonate portion of the rocks is represented by normal dolomite. Barite and gypsum often occur in the vesicules.

Despite comparatively good studies of the structure of dolomite-containing strata and the material composition and structural-textural features associated with the dolomitic rocks of the Belorussian reef [1, 15], the facies-paleogeographical environments of carbonate accumulation in Pinsk and Lapichsk times and also the physicochemical conditions and the time of dolomite formation remain unclarified for the most part. Various opinions have been

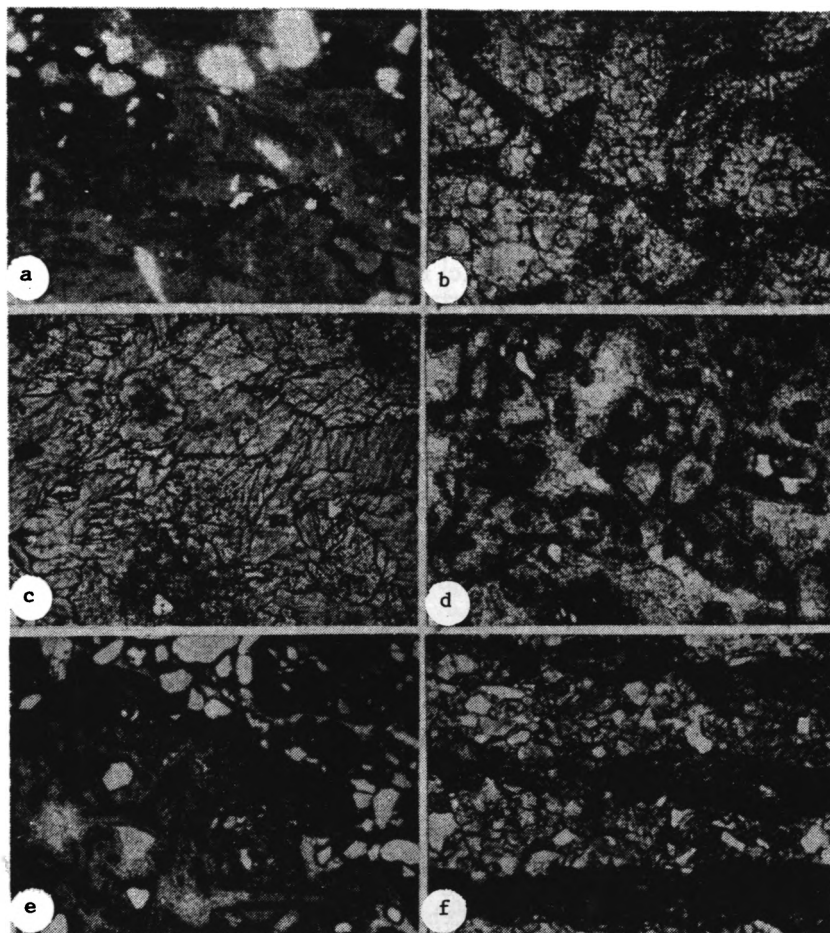


Fig. 3. Microphotography of rocks of the Lapichsk Suite: a) microgranular dolomite with stylolitic joints filled with iron oxides and clay minerals (drillhole Osipovich-7, depth of 550.3 m, 80 $\times$); b) dolomitic authigenic breccia; fragments) very fine- and fine-grained dolomite, cement) microgranular (drillhole Osipovich-14, depth of 773.0 m, 40 $\times$); c) intermediate- and coarse-grained dolomite (drillhole Osipovich-14, depth of 772.0 m, 40 $\times$); d) fragmental-microphytolithic dolomite (drillhole Osipovich-5, depth of 557.0 m, 40 $\times$); e) microphytolithic dolomite: black) microgranular dolomite pigmented with iron oxides, grey) very fine- and fine-grained dolomite, white) detrital quartz (drillhole Osipovich-7, depth of 546.0 m, 40 $\times$); f) silty dolomite, very fine and fine-grained with feldspathic-quartzitic clastic material (drillhole Osipovich-14, depth of 763.5 m, 40 $\times$).

offered concerning this conclusion. In particular, the dolomite in the rocks of the Lapichsk Suite are believed to be for the most part secondary, predominantly catagenetic. Since, one can find in this suite, interlayers of fairly pure dolomites and sandstones with abundances (basal type) of dolomitic cement showing no signs of corrosion of the clastogenic material (see Fig. 2a, b, c, d, and f), rocks in which the formation of dolomite cannot be satisfactorily explained by the processes of catagenesis, the suite has come to be considered primary-sedimentary.

With regard to the dolomites of the Lapichsk Suite, which usually have been considered as primary-sedimentary or even possibly in part secondary (diagenetic), the point of view that they are of endogenic origin has attained popularity in recent years [5, 22, 23]. Based on the high contents of manganese, strontium, and barium in individual varieties of dolomites, the presence of a heavy fraction obtained from two samples of brecciated dolomites, angular grains of monoclinic and orthorhombic pyroxenes, amphibolites, olivine, pyropes, chromespinels,

and also the interpretation of several phytolithic and breccialike microtextures of dolomites as relict tuff structures (see Fig. 3d), K. E. Yakobsen arrived at the conclusion that a significant portion of the dolomites of the Lapichsk Suite are dolomitic or are dolomitized carbonatites and carbonatite tuffs. For this reason, he allows for the possible presence of related carbonatite formations, kimberlites, in the region where deposits of the Lapichsk Suite are present and gives recommendations for prospecting in this regard.

Equivocal treatment of the origin of the dolomitic rocks of the Belorussian reef has occasioned a number of major disagreements on questions of the genesis of the rocks, their stratigraphic correlation, and the stratigraphic reconstructions and conclusions based upon such correlations [13, 15, 18, 22].

The controversy surrounding the dolomites and dolomite-containing rocks of the Belorussian reef and the paleogeography associated with the corresponding stages of sediment accumulation is, to a significant degree, a reflection of the state in which one of the most controversial problems of lithology, the problem of dolomite formation in the Precambrian, finds itself. One of the important methods for reconstructing the facies-paleogeographic environments of carbonate deposition and establishing the origin of carbonate rocks of the Phanerozoic is bio- or ecologico-facies analysis. In combination with lithological methods, it allows one to fairly confidently answer questions concerning the genesis, facies, and formational classification of carbonate rocks and provides specific predictions for oil exploration and other operations.

A more complex problem concerns questions of facies analysis and genesis of carbonate rocks (especially dolomites) of the Cryptozoic and, in particular, the Upper Proterozoic. In contrast to Phanerozoic rocks, rocks of the Precambrian are almost devoid of paleontological remains. Therefore, the possibilities for bio- or ecologico-facies analysis of the conditions of carbonate accumulation, especially dolomite formation, are extremely limited in the Precambrian. As a rule, this has led to controversial conclusions. The data of lithological facies analysis are not always unequivocal, in view of the widespread occurrence of postsedimentary alterations in the carbonate rocks of the Precambrian. These alterations effect to one degree or another, and often almost completely change, the primary structures, textures, and sometimes mineral compositions of the rocks. The comparative lithological method is not applicable here, since the paleogeographic and physicochemical conditions associated with sedimentogenesis in the Precambrian (the compositions of the hydrosphere, the atmosphere, the role of the biogenic factor, etc.) differed substantially from those during the Phanerozoic [8].

The circumstances mentioned impels the use of geochemical and other nontraditional methods for studying carbonate rocks for our purposes [3, 8, 16, 20]. The present report concerns a first attempt at a detailed investigation of the dolomitic rocks of the Belorussian reef. We investigated the distribution of concentrations of strontium, a number of minor and trace elements, carbon and oxygen isotopes, and the composition of clastic minerals in dolomites and dolomitic-clastogenic rocks of the Pinsk (46 samples) and Lapichsk (28 samples) suites at almost all sites of their occurrence and within different structural-facies zones (see Fig. 1).

Manganese. In samples we analyzed from the dolomite-containing rocks of the Pinsk Suite (the major portion of which consisted of sandstones with dolomitic cement and sandy dolomites), the MnO content ranged from 0.04 to 1.66% (Table 1). This significant variation in manganese content is due to differing concentrations of dolomite in the rocks (from 5-10 to 50-70%, up to 90-95% in individual samples). The high coefficients of linear correlation of manganese with calcium and magnesium (from 0.80 to 0.98 at different inspection sites) and the inverse dependence between contents of MnO and Al_2O_3 are evidence of this.

In dolomites and dolomitic-terrigenous rocks of the Lapichsk Suite with significantly higher concentrations of the dolomitic component than are found in the rocks of the Pinsk Suite, values of 0.2-0.5% predominate for variations in MnO content from 0.14 to 1.25%. These values are similar to the average values for MnO content (0.11%) in reef dolomites of the Eastern European platform [16]. The elevated (up to 0.8-1.25%) contents of MnO characteristic of red (ferruginous) vesicular dolomites are due to their secondary enrichment with manganese in the zone of hypergenesis, where selective removal of calcium and magnesium takes place. Manganese, being a less mobile element, is concentrated in weathered crust, is partially transported through the weathered crust to lower horizons, and is fixed in the cracks

TABLE 1. Chemical and Isotopic Composition of Dolomites and Dolomite-Containing Rocks of the Belorussian Reef

Drillhole	Depth, m	Content								$\delta^{18}\text{O}_{\text{CPDB}}$ ‰	$\delta^{18}\text{O}_{\text{SMOW}}$ ‰
		SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	Sr		
1	2	3	4	5	6	7	8	9	10	11	12
Lapichsk Suite											
Osipovich-5	547.0	3.1	0.2	0.6	1.25	20.4	30.6	0.1	120	2.2	-6.1
Osipovich-7	546.5	12.1	1.1	2.0	0.76	17.9	26.0	0.9	370	0.5	-7.5
	546.7	3.1	0.3	1.3	0.37	19.8	31.0	0.3	410	0.2	-
	550.0	25.2	1.9	1.5	0.75	16.3	23.0	1.3	45	1.8	-10.4
	550.5	10.6	1.3	1.5	0.98	18.0	26.3	0.8	140	-0.2	-6.7
	550.6	0.7	0.1	0.6	0.80	19.5	32.5	0.1	200	0.4	-
	550.7	26.0	2.8	2.6	0.79	12.7	20.7	2.0	85	0.4	-
Osipovich-9	703.0	3.4	0.5	1.0	0.48	18.9	30.3	0.2	900	2.1	-
	704.0	1.0	0.1	1.2	0.37	19.4	31.8	0.1	850	0.8	-
	704.1	2.0	0.1	1.0	0.24	18.9	30.6	0.1	670	1.7	-
	712.5	1.9	0.2	1.2	0.38	21.0	31.2	0.1	320	1.1	-
Osipovich-12	700.0	2.4	0.3	1.7	0.18	21.2	30.9	0.2	450	2.7	-14.7
	700.1	4.1	0.6	1.7	0.16	18.5	29.8	0.4	270	2.4	-
	740.0	17.0	0.7	1.3	0.48	16.2	25.5	0.5	300	1.5	-
	740.1	7.6	0.7	0.7	0.49	15.5	27.9	0.3	450	1.3	-
Osipovich-14	714.0	36.3	1.5	2.0	0.35	14.7	19.4	0.1	40	0.0	-8.4
	714.1	3.5	0.4	1.8	0.33	18.4	29.7	0.3	250	0.3	-
	714.2	13.1	1.2	2.0	0.37	16.6	24.6	1.0	170	1.0	-
	714.3	24.7	1.5	0.6	0.34	15.6	21.7	1.4	160	0.2	-
	763.5	6.2	0.7	1.6	0.35	20.0	28.9	0.4	450	3.4	-12.1
	771.7	10.3	1.0	0.6	0.17	20.2	27.4	0.7	390	3.9	-8.7
	772.0	11.0	1.3	0.8	0.26	19.3	27.1	0.6	500	3.0	-4.6
	772.1	5.9	0.6	0.3	0.14	19.0	28.3	0.5	1100	3.0	-
	773.0	1.2	0.2	0.4	0.16	22.6	31.7	0.0	900	1.9	-10.7
	657.0	0.3	0.0	1.8	0.17	19.6	30.2	0.0	850	0.2	-
Osipovich-82 Rogachev-1	642.0	53.3	4.2	3.4	0.24	9.3	10.8	2.5	50	-0.6	-
	644.5	10.4	8.8	2.4	0.38	17.3	25.5	0.7	45	-1.7	-3.3
	647.0	54.5	3.2	2.7	0.23	9.5	11.8	2.1	30	-0.4	-7.5
Arithmetic average		12.5	1.3	1.4	0.43	17.7	26.6	0.6	376	1.2	-8.4
Standard deviation		14.8	1.8	0.8	0.28	3.2	5.6	0.7	308	1.3	3.2
Pinsk Suite											
Borushevsk-2	1580.0	89.5	4.5	0.4	0.04	1.3	1.3	1.8	35	-7.0	-13.1
	1607.0	73.0	8.7	0.8	0.14	5.1	4.6	4.1	95	-	-
	1629.0	67.7	8.5	1.5	0.10	6.4	6.0	3.2	60	-1.3	-12.7
	1649.5	53.7	6.3	1.5	0.19	9.1	10.9	2.7	150	-1.7	-10.1
	1660.0	65.0	6.8	1.1	0.07	7.1	8.2	2.7	35	-4.4	-7.9
	1663.0	80.7	5.9	1.5	0.11	2.1	3.3	3.8	100	-4.9	-
Rogachev-1	662.0	68.7	4.2	1.8	0.35	6.9	7.9	2.1	30	-5.7	-
Cherven'-3	289.0	59.9	5.5	2.4	0.67	8.6	9.8	2.6	170	-4.0	-9.2
	308.0	19.7	2.2	1.4	1.22	16.0	23.9	1.2	280	-1.5	-6.7
	311.0	61.0	3.7	1.3	0.56	7.9	8.7	2.0	200	-3.3	-
	360.0	75.6	5.2	1.1	0.43	6.1	6.5	2.8	70	-4.2	-
Cherven'-4	393.0	24.0	4.0	1.4	1.29	15.1	21.0	1.9	110	-5.6	-7.4
	417.0	66.5	5.4	1.4	0.55	7.6	8.0	2.8	50	-5.6	-3.1
	417.1	49.6	4.1	1.4	0.60	8.7	15.4	2.6	150	-5.3	-
	428.0	51.5	5.1	1.0	0.51	8.7	14.7	2.9	80	-	-
	436.0	54.7	6.0	1.3	0.43	7.1	12.7	3.3	90	-4.2	-
	444.0	61.4	4.3	1.7	0.34	7.0	12.7	2.1	50	-	-
	450.0	74.6	5.5	0.4	0.15	4.3	7.4	3.8	85	-4.0	-
	451.0	61.2	6.2	1.2	0.70	8.9	9.0	3.3	95	-3.6	-
	461.0	54.5	4.5	1.1	0.18	8.6	14.3	2.7	60	-	-
	468.0	29.0	4.0	1.1	1.11	15.9	21.0	1.6	50	-2.0	-
Nesvizh-41	155.0	58.6	8.4	3.0	0.46	5.9	11.0	3.5	150	-4.0	-

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
Slutsk-5	283,0	2,0	0,2	0,5	1,12	19,7	31,4	0,2	120	-2,4	-5,4
	283,1	33,6	2,1	1,2	1,01	14,4	20,9	1,3	120	-1,6	-6,8
	286,0	59,9	5,6	2,0	0,51	7,6	9,1	3,3	70	-2,9	-4,5
	371,0	60,6	5,1	3,0	0,37	6,6	8,3	2,8	70	-1,4	-7,2
	371,1	64,5	4,4	1,8	0,37	7,0	8,3	2,4	170	-2,2	-3,9
Slutsk-22	202,0	56,6	5,0	0,8	0,66	8,5	11,1	3,1	110	-1,6	-6,8
Zhitkovich-03	330,0	60,0	5,1	2,1	0,31	8,6	10,1	1,7	80	-3,2	-9,2
	334,0	60,6	4,0	1,5	0,26	8,4	9,1	2,0	120	-4,8	-11,2
	346,0	61,1	4,3	1,0	0,35	9,6	10,3	1,7	70	-2,2	-1,3
	350,0	64,7	3,5	1,2	0,25	8,5	9,5	1,8	85	-2,6	-
	382,1	71,9	2,4	0,6	0,33	6,8	8,4	0,9	60	-	-
	384,1	35,6	2,5	0,9	0,66	14,2	19,6	1,6	70	-	-
Zhitkovich-080	397,5	61,1	4,1	0,8	0,56	2,1	16,0	2,3	150	-7,6	-7,2
Zhitkovich-380	202,0	30,2	1,4	2,5	1,66	14,4	22,0	0,6	140	-0,6	-
Zhitkovich-390	355,0	75,7	1,3	0,7	0,24	6,4	7,7	0,5	85	-3,3	-9,4
	361,0	37,4	4,2	1,8	1,53	12,7	18,7	1,6	95	-1,5	-9,8
Pinsk-15	188,0	58,9	4,6	1,1	0,28	7,5	13,0	2,3	90	-4,2	-
	335,0	64,7	2,0	0,4	0,26	7,9	13,3	1,3	115	-2,2	-
	335,1	71,2	1,3	0,2	0,26	6,9	12,8	0,8	110	-3,2	-
Pinsk-22	255,0	72,2	1,3	0,2	0,37	6,6	12,0	0,9	45	-2,2	-
	255,5	1,1	0,2	0,1	0,46	20,2	32,8	0,1	240	-1,9	-
	255,6	3,5	0,7	0,2	0,49	18,9	31,8	0,4	250	-2,0	-
Pinsk-24	640,0	63,7	7,4	1,3	0,24	6,4	8,6	2,7	45	-2,7	-
Pinsk-29	413,0	63,1	6,3	1,4	0,33	5,9	9,6	2,9	60	-4,1	-
Arithmetic average		55,1	4,3	1,2	0,50	8,9	12,9	2,1	104	-3,3	-7,6
Arithmetic average		20,4	2,1	0,7	0,38	4,4	7,2	1,0	57	1,6	3,1

Explanation. The determination of SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , and K_2O (wt. %) was carried out by the quantitative x-ray spectral method on a SRM-18 instrument (L. F. Gulis, analytical chemist), Sr (g/ton): by the quantitative spectral method (L. F. Gulis, analytical chemist); ^{13}C , ^{18}O : on a MI-1301 mass spectrometer, from carbonic acid gas extracted by breaking down dolomite with orthophosphoric acid (V. M. Kolkovskii and I. L. Kolosov, analytical chemists). The analyses were carried out at the Institute of Geology and Geochemistry of the Academy of Sciences of the USSR.

and intergranular spaces along with iron hydroxides. This was confirmed by microprobe studies of light-grey massive (without clear indications of hypergene alterations) and red vesicular dolomites. The Mn incorporated into the dolomite lattice was distributed fairly evenly in the first type of rock. Besides the isomorphic incorporation into dolomite, a major portion of the Mn coincided with intergranular seams of dolomite in the second type of rock.

Thus, significant portions of the manganese in dolomitic and dolomite-containing rocks of the Pinsk Suite and in rocks of the Lapichsk Suite unsubjected to secondary reworking of this element are bound with the carbonate component, i.e., with mineral dolomite.

A comparison of the magnitude of MnO/MgO , reflecting the manganese content within the dolomitic component of these rocks, indicates that the ratio is 2-3 times greater in Pinsk dolomites than in Lapichsk dolomites.

The authors explain the high contents of manganese in the dolomite of the Pinsk rocks by sedimentary, and possibly in part diagenetic dolomite formation in a shallow-water epicontinental basin during a period when the basin was subsiding and undergoing partial drying out over a large portion of the near-shore facies. It is known that 40-60% of the manganese

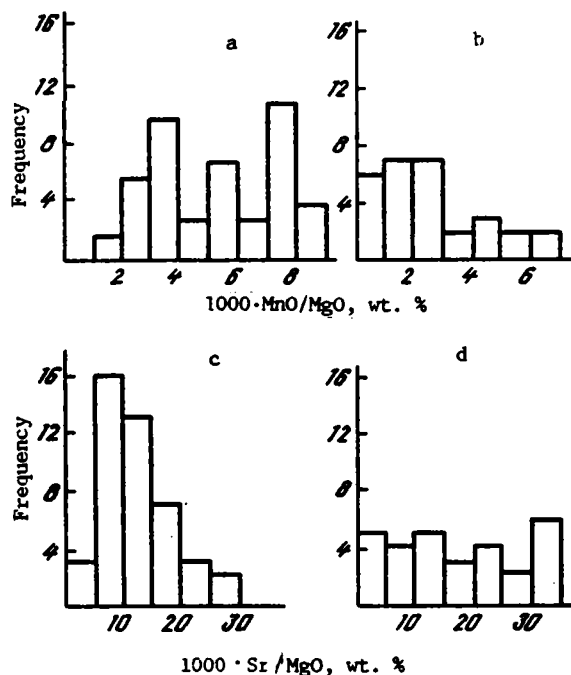


Fig. 4. Diagram of the distribution of the contents of manganese and strontium in dolomitic rocks of the Pinsk (a, c) and Lapichsk (b, d) Suites of the reef.

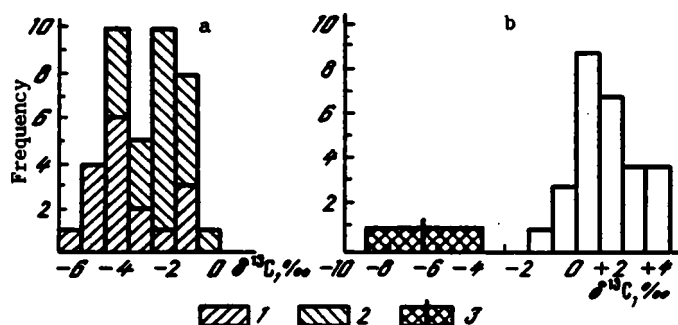


Fig. 5. Diagram of the distribution of ^{13}C in dolomitic rocks of the Pinsk (a) and Lapichsk (b) Suites of the reef. 1) Central, 2) southern region, 3) carbonatites (vertical bars: average value of ^{13}C [7]).

dissolved in fresh continental waters is precipitated in the near-shore zones of marine basins [10]. The primary source of this element in the dolomites of the Pinsk Suite was weathered crusts in the crystalline rocks of the Belorussian and Voronezhsk massifs. The constant supply of manganese during the slow accumulation of dolomite in the shallow-water, periodically drained basin facilitated isomorphic incorporation of significant quantities of this element into the lattice of the dolomite.

This conception of the genesis of the dolomitic and dolomite-containing rocks of the Pinsk Suite, based upon geochemical, structural-textural features of these rocks and their position in the suite's section, is a physicochemical agreement with a model of primary-sedimentary dolomite formation during mixing of fresh hydrocarbonate-calcium and marine waters [11].

A content of MnO in the Lapichsk dolomites similar to the average content in dolomites of the reefs of the Eastern European Platform and the presence of phytolithic varieties of dolomites does not contradict conceptions of an alteration of deposits of the Lapichsk Suite in a sedimentary basin with a normal, periodically elevated salinity and a significant role for biogenic carbonate material usually depleted in manganese [3]. The established global

TABLE 2. Content of Microelements in Dolomites and Dolomite-Containing Rocks of the Upper Proterozoic of Belorussia, g/ton

Elements	Pinsk Suite			Lapichsk Suite		
	no. of analyses	average arithmetic content	standard deviation	No. of analyses	average arithmetic content	standard deviation
Ti	43	1352,3	1218,6	28	311,2	297,4
V	43	27,6	21,3	28	25,4	15,1
Cr	43	17,4	6,8	28	5,8	8,0
Co	43	4,3	3,1	28	2,4	1,7
Ni	43	8,2	2,2	28	5,8	2,6
Cu	30	30,5	22,7	14	4,1	2,5
Y	30	46,0	32,4	14	18,3	10,2
Zr	43	178,4	113,4	28	78,9	60,1
Nb	30	13,2	8,4	14	3,4	3,0
Yb	30	2,8	2,0	14	0,9	0,8

Explanation. Statistically processed quantitative spectral analysis carried out at the Institute of Geology and Geochemistry of the Academy of Sciences of the BSSR; A. D. Narodetskaya and B. E. Ostrovskaya, analytical chemists.

pattern of high content of this element in middle-reef carbonates and in upper-reef carbonates [20] corresponds to a time of higher manganese content in the dolomites of the middle-reef Pinsk Suite relative to the dolomites of the Lapichsk (upper or terminal reefs).

Strontium. The strontium content (see Table 1) in the samples of dolomites and dolomite-containing rocks of the Pinsk Suite which we studied ranged from 30 to 250 g/ton (an average of 100 g/ton). The major portion of the strontium is bound with the dolomitic component of these rocks. This is evident from the results of the analyses presented and is also confirmed by calculations of the coefficients of linear correlation between Sr and contents of Mg and K. The first correlated pair reflect the binding of strontium with dolomite; the second pair reflect the binding of strontium with feldspars and hydromicas. In the rocks of the Pinsk Suite in the southern regions, the correlation coefficient for Sr with Mn equals 0.66; that for Sr with K equals -0.58. In the central regions, these correlational relationships are less close. This is apparently due to the large carbonate of noncarbonate material in the rocks.

In the rocks of the Lapichsk Suite, Sr contents from 40 to 1100 g/ton (an average of 420 g/ton) have been found. The major portion of this Sr is also bound with dolomite. The positive correlational relationship between Sr and Mg contents and the negative relationship between Sr and K (correlation coefficients of 0.55 and -0.48, respectively) are evidence of this.

A review of a large amount of data on strontium in carbonate rocks of various ages and origins indicates that the content of this element in diagenetic dolomites amounts to $n \cdot 10$ g/ton [21]. The Sr content decreases from $n \cdot 100$ to $n \cdot 10$ g/ton during dolomitization of limestones. At the same time, Sr is present in quantities of up to 1000 g/ton or more in evaporite deposits. It is also known that the value of $1000 \cdot \text{Sr}/\text{Ca} > 0.5$ in the diagenetic and sedimentary dolomites of the near-shore facies while it does not exceed 0.3 in the catagenetic facies [20]. An Sr content equaling 200-750 g/ton (approximately 400 g/ton on an average) is characteristic of the mid-upper-reef dolomites of the Yenisei range, which are considered to be sedimentary and diagenetic.

The predominance of strontium concentrations greater than 300 g/ton and values of $1000 \cdot \text{Sr}/\text{Ca} > 0.5$ in the samples analyzed from the Lapichsk Suite confirm a primary-sedimentary origin for a major portion of the dolomite in this suite. A content of this element greater than 600 g/ton is evidence of periodic salinization of the Lapichsk basin. The sedimentary and possibly in part diagenetic genesis of the dolomites of the Pinsk Suite is directly confirmed by the predominance of values of $1000 \cdot \text{Sr}/\text{Ca} > 0.6$ within them [20].

Thus, the analysis of the results obtained indicates that practically all of the Mn and at least a major portion of the Sr in the dolomites and dolomite-containing rocks of the

pinsk and Lapichsk Suites are bound with the carbonate component, i.e., with mineral dolomite. The published data is evidence of this [3, 19-21]. Therefore, neither the percentages nor weights of their quantities in the samples analyzed are most representative for comparing contents of elements in the Pinsk and Lapichsk dolomites. The quantities MnO/MgO and Sr/MgO are best for this purpose (Fig. 4). They indicate that the content of Mn is higher and the content of Sr lower in the dolomitic material of the rocks in the Pinsk Suite than in the Lapichsk. In this case, the contents of both elements, both in the Pinsk and in the Lapichsk dolomites, vary in approximately identical fashion both along the section and laterally. This is apparently due to the appreciable inhomogeneity and instability of the facies conditions during Lapichskian times (transient salinization of the basin of sediment accumulation, the presence of algal structures within the basin, etc.) and is confirmed by the great variety of structures, textures, rock compositions, and make-up of section noted above. Also, we do not exclude the possible influence of secondary reworking of these elements in the zone of hypergenesis.

The contents of Co, Ni, Cr, V, Cu, Ti, Y, Nb, and Yb (Table 2) in the dolomites and dolomitic rocks of the Pinsk and Lapichsk suites are within the clarke ranges for sedimentary rocks of the corresponding types [9].

The correlational analysis indicates that the major quantities of these elements in the rocks of the Pinsk Suite, among which titanium predominates (average content of 1352.3 g/ton), are found with the clayey matter of the rocks. Their close correlation with potassium is evidence of this. Ni, Co, Cu, V, Y, and Yb correlate well with Ti.

The rocks of the Lapichsk Suite are characterized by lower Ti content (by a factor of 4.5 on an average) than the rocks in the Pinsk. The Cu content averages 7 times lower, and the remaining elements, with the exception of Nb, average 1.5-3 times lower.

Isotopes of Carbon and Oxygen. We carried out the 40 isotopic analyses of rocks of the Pinsk Suite and 28 of the Lapichsk Suite (the first for the territory of Belorussia) in order to study the isotopic composition of the carbon and oxygen of the reef dolomites. Predominantly unaltered (without clear indications of hypergene or other secondary transformations) dolomites and dolomitic-clastogenic rocks containing from 15 to 98% normal dolomite with various degrees of crystallinity were analyzed.

It was found that the dolomite in all of the samples analyzed from the Pinsk Suite is characterized by negative $\delta^{13}\text{C}$ values, while the dolomite of the Lapichsk Suite, with individual exceptions, shows positive $\delta^{13}\text{C}$ values. These values vary from -0.6 to -7.6‰ for the Pinsk dolomite (-2 to -5‰ predominates). They vary from +0.2 to +3.9‰ for the Lapichsk dolomite. Several negative (-0.2 to -0.6‰ and one -1.7‰) values of $\delta^{13}\text{C}$ obtained for the Lapichsk Suite are apparently due to a disturbance of the original ratio of carbon isotopes in dolomites which underwent hypergene transformations: leaching with the participation of atmospheric carbon dioxide, silification, and also catagenetic dolomite formations.

The distribution of analytical values of $\delta^{13}\text{C}$ similar to a normal distribution (Fig. 5, the similarity of the control determinations, and the clear differentiation with respect to suites noted above indicate the reliability of the results obtained. When taking into account the published data on isotopic composition of carbon in carbonate rocks of various origins and ages [4, 6, 7, 17, 20], they allow one to analyze these results in two aspects: genetic and chronological.

It is evident from Fig. 5 that $\delta^{13}\text{C}$ is higher in the dolomites of the Lapichsk Suite than in the dolomites of the Pinsk Suite by 4.5‰ on an average. The maximum difference is 11.5‰. Together with the existing geological data and the geochemical data presented above, this is evidence for the formation of the Pinsk and Lapichsk dolomites in sedimentary basins of different types, with substantially different facies-paleogeographic environments and mechanisms of dolomite formation.

The low carbon of the isotope ^{13}C in the dolomites of the Pinsk Suite is apparently due primarily to the formation of the dolomites in a broad, shallow-water basin in a "light" atmosphere of carbon dioxide. The active hydrodynamic regime of the basin prevented isotopic equilibrium between the CO_2 of the atmosphere (with negative values for $\delta^{13}\text{C}$) and the HCO_3^- and CO_3^{2-} of seawater (with high values of $\delta^{13}\text{C}$ in comparison to those for the CO_2 of the atmosphere) from being reached in the system [4, 20]. Under such conditions, this led to the incorporation of carbon relatively impoverished with regard to ^{13}C into the lattice of the

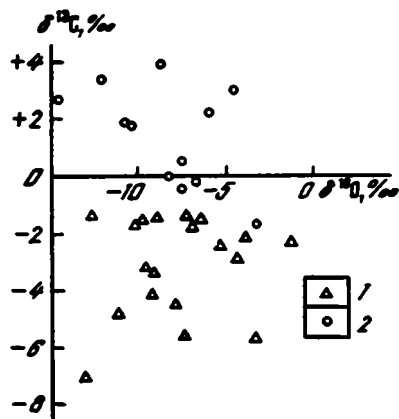


Fig. 6. Variation in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ within the dolomitic rocks of the Pinsk (1) and Lapichsk (2) Suites of the reef.

dolomite formed. The explanation for the peculiarities associated with the isotopic composition of the Pinsk dolomites is in complete agreement with conceptions of the Pinsk basin and its facies environments based upon lithological criteria (ubiquitous traces of mixing and scouring of sediments, intraformational breaks, structural-textural peculiarities of the rocks, their primary coloration, etc.) and data from geochemical investigations.

The sharply predominating positive values of $\delta^{13}\text{C}$ in dolomites of the Lapichsk Suite together with the recurring lithologic and geochemical characteristics of these rocks allow us to conclude that dolomite formation occurred in a relatively small isolated sea basin which had conditions for arriving at isotopic equilibrium in the " CO_2 atmosphere- HCO_3^- - CO_3^{2-} -seawater" system. The highest value of $\delta^{13}\text{C}$ (+3 to +3.9‰) together with the presence of diagenetic or, possibly early-catagenetic barite and gypsum in the Lapichsk dolomites are evidence of sporadic salinization of the basin [4, 7, 20]. The high content of the isotope ^{13}C in the Lapichsk dolomites could partly be due to a significant participation of blue-green algal colonies in their formation. This follows from consideration of the isotopic equilibria [2] and is confirmed by the results of an isotopic study of the carbonate rocks of the Cambrian in Eastern Siberia [6]. It is logical to suggest that the periods of the most luxuriant development of blue-green algae and algal dolomite formation coincided with periods of aridization combined with draining of the Lapichsk basin, the shrinkage of saline lagoons, and the formation of algal banks, bioherms, and biostromes.

The chronostratigraphic allocation of 1931 designed to determine the isotopic composition of carbon in various aged sedimentary carbonate rocks of the earth and presented in a report [20] shows that the quantity $\delta^{13}\text{C}$ in the middle-reef dolomites is 3-4‰ less than in the upper-reef dolomites (with average values of approximately -2.5 and 1.5‰, respectively). The data obtained on the isotopic composition of the carbon in the dolomites of the Pinsk and Lapichsk Suites, suites which we have assigned to the middle and upper (terminal) reef, correspond to the following pattern on the basis of geological and other criteria: $\delta^{13}\text{C}$ in the Lapichsk dolomites averages 4.5‰ higher than in the Pinsk dolomites. In this case, the greatest difference in isotopic composition of carbon (>5‰) was noted in dolomites from closely located sections of the Pinsk and Lapichsk suites in the central part of Belorussia (the Osipovichei-Chervenya region; see Figs. 1, 5a), where these dolomites are considered to be stratigraphic analogs by several authors [18]. Regardless of the nature of this distinction, which apparently is the combined outcome of a number of factors, it can be considered as still another illustration of the diversity of the Pinsk and Lapichsk Suites and the correctness of assigning the first to the middle and the second to the upper reef.

In Fig. 6, illustrating the variation in isotopic composition of carbon and oxygen (as determined in the very same samples), it is evident that the values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for the rocks of the Pinsk and Lapichsk Suites form almost nonoverlapping fields because of the differences in the isotopic composition of carbon. The dolomitic rocks of these suites are practically indistinguishable on the basis of the isotopic composition of the oxygen. This explains their long post-sedimentational history (more than a million years for the Pinsk dolomites and more than 0.6-0.7 million years for the Lapichsk dolomites), over the course of which the oxygen in the dolomite could enter into an isotopic exchange with the oxygen of the ground waters and the gases dissolved in them. It is known that the isotopic composition of the oxygen in carbonate rocks can be disturbed more easily and to a greater degree than can that of carbon [4]. Our results confirm this.

In the vesicular recrystallized dolomites of the Lapichsk Suite, $\delta^{13}\text{C}$ decreases by 1-2‰ in comparison with the massive very fine- and fine-grained dolomites; $\delta^{18}\text{O}$ decreases by 4-5‰. An analogous tendency was noted for the dolomitic rocks of the Pinsk Suite.

Clastic Minerals. Practically all of the dolomitic and dolomite-containing rocks of the Pinsk Suite and a significant portion of the Lapichsk rocks include catagenetic material: from small (5-10%) admixtures to 90%. Quartz predominates in the composition of the light fraction of these rocks. Feldspars (10-20%) and fragments of siliceous rocks (5-10%) are present in subordinate quantities. Differences with respect to the quantitative ratios of these minerals in the rocks of the Pinsk and Lapichsk suites are not substantial: There are somewhat more rock fragments in the first and more feldspars in the second. In general, the clastogenic material of these rocks is fairly mature from a lithological standpoint (75-85% consists of quartz). This description is corroborated by the corresponding composition of the heavy fraction. In the rocks of the Pinsk Suite, the clastogenic material is represented by associations of stable minerals which maintain high concentrations along the section and over the area: ore minerals (ilmenite, titanomagnetite, and hematite), zircon, tourmaline, and apatite. The heavy-mineral fraction in the Lapichsk Suite is somewhat richer. In addition to the predominate ore minerals, zircon, tourmaline, and apatite, they also contain garnet (sometimes in quantities comparable to those of the minerals just mentioned) and staurolite. Rutile and monazite are present in sparse and isolated grains with the rocks of both suites. The differences in the composition of clastic accessory minerals in the dolomitic and other rocks of the Pinsk and Lapichsk Suites, in the first place, allows their stratigraphic identification even under circumstances when such rocks are similar with respect to macroscopic indicators (structure, texture, color) and composition of primary rock-forming components. In the second place, such differences constitute still another bit of evidence concerning the diversity of the Pinsk and Lapichsk Suites.

The mineral compositions of the clastogenic cement of rocks in the Pinsk and Lapichsk Suites which we have described and which were established 60-70 years ago [1, 12, 15] are completely confirmed by our investigations.

In connection with the research of Yakobson [22, 23], in which a different composition was suggested for the heavy-mineral fraction in the Lapichsk dolomites and on the basis of which conclusions were drawn concerning endogenous (carbonatite) origin of the dolomites, we decided to carry out additional mineralogical investigations of these rocks. The heavy fractions were isolated from residues insoluble in 10% acetic acid taken from 13 samples of dolomites with characteristic phytolithic and breccia-like microstructures, which Yakobson interprets as relict ash structures of carbonatite tuffs. Mineralogical investigation of these fractions completely corroborated the composition of accessory minerals in the rocks of the Lapichsk Suite as described above. Not a single grain of olivine, pyroxenes, chromespinels, or any of several other minerals reported in [22, 23] were found in any of the fractions we studied.

The geochemical, isotopic, and mineralogical investigations of the dolomitic and dolomite-containing rocks of the Pinsk and Lapichsk Suites of the Belorussian reef allow us to draw the following conclusions when taking into account data on the geology and lithology of these suites [1, 15].

1. The dolomitic and dolomite-containing rocks, together with the clastogenic rocks closely associated with them and predominating in the section of the suites mentioned, accumulated in epicontinental marine basins of various types. Dolomite formation during Pinskian times took place under the conditions of the near-shore facies of a broad, shallow-water basin predominantly during periods when the basin was draining and fresh continental waters were mixing with seawater. During Lapichskian times, dolomite formation took place in a closed, periodically salinated basin and in near-shore lagoons by chemogenic and biogenic (due to the activities of colonial blue-green algae) precipitation of dolomite from seawater.

2. The Lapichsk dolomites have nothing in common with carbonatites with respect to isotopic composition of carbon, content of manganese and strontium, composition of light and heavy fractions of clastic minerals, and also other lithological features and are ordinary sedimentary rocks.

3. Features associated with the distribution of manganese, carbon isotopes, the composition of the heavy fraction in clastic portion of the rock confirm the idea of diversity in the Pinsk and Lapichsk Suites and lead to assigning the Pinsk Suite to the middle reef and the Lapichsk Suite to the upper reef.

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The lithology of tobacco ores of the Kerch iron ore deposit is studied. The mineral composition of the oolites and the cementing mass is investigated. A comprehensive analysis is made of trioctahedral ferruginous smectites, which are "instantly" converted by oxidation to dioctahedral Fe-smectites. The possibility of micatization of these smectite minerals is demonstrated.

The mineralogy and genesis of Kerch iron have been studied for many years by N. I. Andrusov, N. Ya. Andreeva, N. E. Efremov, M. I. Kantor, A. U. Litvinenko, V. F. Malakhovskii, P. I. Naumenko, A. V. Sidorenko, L. O. Stankevich, N. M. Strakhov, F. V. Chukhrov, E. F. Shnyukov, Yu. Yu. Yurk, L. K. Yakhontova, et al. However, no commonly accepted theory on the origin and mineral composition of these ores has emerged. Recently, the Geological Institute of the Academy of Sciences of the USSR developed a new approach to the study of natural entities, geomineralogy, which is based on a comprehensive investigation of natural objects. It includes a description of the general "geological situation" in terms of geologic formations and facies, as a background for describing the material composition of rocks, the paragenetic mineral associations, and fine structural and crystallochemical investigations of the main minerals, whose indicator characteristics may reflect the rock formation and alteration history [14]. The comprehensive geomineralogic methodology has been applied to studies of clastogenic rocks [6], biogenic-chemogenic rock complexes [8], and clastogenic-evaporitic rocks [12]. In the present paper this methodology is applied to iron ore deposits.

The Kerch iron ore deposits in the eastern part of the Kerch Peninsula are an element of the extensive Azov-Black Sea iron ore province, which includes Kimmerian ore layers in the Kerch Peninsula, Krasnodar Province, the Azov region, the Sivash area, and Kherson Province, the Azov region, the Sivash area, and Kherson Province [16]. Tectonically, the basin is connected with the Indol-Kuban trough, formed during the Neogene along the perimeter of the meganticlinorium of the Greater Caucasus and the Crimean Mountains, and along the Kerch-Taman subsidence region separating these two Alpine structures. Ore horizons confined to the Middle Pliocene-Kimmerian are underlain by Mesozoic and Cenozoic sediments, starting from the Middle Jurassic, and covered by sand-clay formations of a Kuyalnik and Quaternary age [1, 2, 16]. The lower Sarmatian and Karagan-Chokrak rocks underlying the metalliferous strata include oil in areas adjacent to the iron ore deposits [3]; the region is also a province of intense mud volcano activity, tracing back to the Maikop strata [17].

Shnyukov [16] distinguished four genetic iron ore deposits and manifestation types in the Azov-Black Sea province: Kerch deposits, associated with large brachysynclinal folds; deposits in depressed synclines of the Kerch Peninsula; ore signs of steep slopes of anticlinal folds and the margin of the Caucasian anticlinorium (Krasnodar Province); and ore signs on extensive shallow shoals, widespread on the northern slope of the Black Sea and the Azov-Kuban depressions and on the southern slope of the Azov crystalline shield. In the present paper we study only the first type of deposits, which concentrates most of the commercial reserves of this basin.

Iron ore deposits in the Kerch Peninsula are confined to troughs: Kamysh-Burun, El'tigen-Ortel', and others. These are ore bodies occurring subhorizontally with dip angles of 1-3°, less often 5-7° [2, 16]. Three types of ore are distinguished by tradition - tobacco, brown, and caviar - each with a different morphology, chemistry, and mineralogy [2, 16].

Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 58-73, March-April, 1989. Original article submitted December 29, 1987.

Geological Position of Tobacco Ores

Tobacco ores occur at the base of the ore horizon. They are found unconformably on sand-clay coquina of a Pontian age, or conformably on Lower Kimmerian clays in the central most subsided parts of troughs at depths of 30-50 m. The contacts of tobacco ores with underlying rocks are sharp. Brown ores rim margins of troughs as strips and cover tobacco ores in isolated locations. They vary in thickness from 3 to 25 m. Caviar ores are found on the sides of troughs as lenses at the top of the ore bed. Toward the central parts of troughs they wedge out and are succeeded by brown varieties. The thickness of these ores is 6-12 m [2, 16]. The present paper is concerned with tobacco ores of the Kerch deposit (Fig. 1).

In the tobacco ore section, two horizons are distinguished, with different occurrence conditions and morphology. The lower horizon, 0.2-0.3 m thick, occurs locally in the deepest portions of troughs. The ore in this horizon is greenish-black, massive, glittery, with a cavernous broken surface and spherical inclusions (60-80%); the inclusions are often segregated and form monolithic matter with cement. Isolated mollusk valves and rare tree twigs are found in the ore. The top horizon (3-8 m thick) is described in the lower part of the ore section of all troughs. The transition between the lower and upper horizons is gradual. The ore in the upper horizon is moist and dark-green; it is massive without any pronounced stratification; it is strong and breaks into uneven pieces. Oolites (40-80%) and cement are well identifiable. The oolites vary from 0.2 mm to 0.7 cm (rarely larger than 1 cm). Besides these two components, the ore contains all kinds of mineral and organic inclusions: elongate rounded pebbles of clay-phosphate rocks with some silt material measuring up to 5 cm across; clay-iron ores in fragments of up to 1.5 cm; various terrigenous minerals, including sand and silt quartz grains (up to 2%), with minerals of heavy and light fractions in isolated grains; intact and broken mollusk shells, mammal bone fragments, and stems and branches of land plants. Organic inclusions are unevenly altered: zoo- and phytomorphoses of carbonates (siderite, Mn-siderite, and oligonite) are often observed, as well as iron phosphates (vivianite), and less frequently iron and calcium phosphate (anapaite) and barite. Nonmineralized, slightly coalified fragments of trees and plant detritus are found. Besides these inclusions, carbonate interlayers, veinlets, and micro- and macronodules are relatively common. There are crystals, crystal druses, phosphite veinlets, and barite nodules and aggregates. Iron sulfides are rare (pyrrhotite, smaltite, and pyrite); they form envelopes on oolites and spherical segregates and oolite-cutting veinlets; they often replace vegetable detritus. Realgar is frequent; it occurs in small (up to 1 mm) crystals, crustlets, and patina [2].

Tobacco ores are covered by a complex genetic combination of sediments. These are mostly so-called tobacco clays, which succeed tobacco ores gradually, both in the vertical and lateral directions. Tobacco clay formations are genetically similar to tobacco ores. They contain few oolites (up to 20%), measuring 1-3 mm. The clays are similar to clay rocks, whence their name. The cement of tobacco clays contains small-grained quartz (0.3-0.002 mm; up to 60%) and, rarely, minerals of heavy and light fractions. Numerous pelecypod shells and rare tree branch fragments are found in the rock. Vivianite and siderite are almost ubiquitous and form thin layers and nodules; they also replace organic remains.

Caviar ores are often found on the sides of troughs, stretching from northeast to southwest and occurring directly on tobacco ores with a distinct boundary. These are friable sand rocks with an addition of gravel, cemented loosely with clay-iron cement. The ores consist of fragments of clay-iron rocks (90-95%) enriched in manganese (up to 4% MnO_2) and oolites (5%). The ore exhibits distinct horizontal stratification, often emphasized by abundant pelecypod shells.

Relationships between tobacco and brown ores are complicated. Brown ores consist of several genetic varieties whose contacts with tobacco ores are different: from sharp contacts to embeddings with vertical and lateral transitions. In situ tobacco ore is dark green, as seen in fresh cores from bore holes and in quarry walls. After exposure to air the ore becomes brownish after 2-4 h and develops small drying cracks in detailed lithologic investigations of tobacco ore horizons a substantial difference was observed in composition of oolites and cement (in the air, oolite color changes faster than the color of the cement by an order of magnitude). Visually, the oolites do not display a concentric structure. Concentric lines in the oolites appear only when they are oxidized. All oolites are round and flat. There are no oriented oolites. Some contain exotic inclusions (large thick-

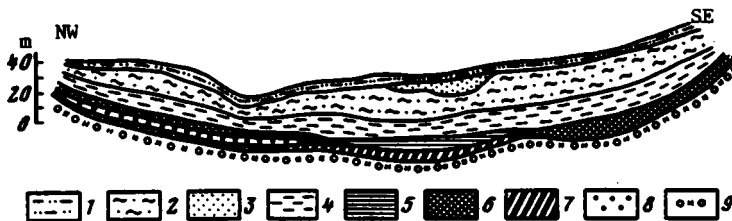


Fig. 1. Geological profile of the El'tigen-Ortel' deposit: 1) limey loam (Q); 2) sandy clay (N_2ku); 3) quartzose sand (N_2ku); 4) gray clay (N_2k_3); 5) tobacco clay (N_2k_3); 6-8) ore (N_2k_2) [6) brown, 7) tobacco, 8) caviar]; 9) sand-clay coquina (N_2p).

walled pelecypod shells from relatively shallow-sea conditions on shellstone, less often sand grounds, as well as gastropods, river crayfish remains, branches and stems of land plants, and flattened pebbles of clay-ferruginous and clay-phosphate rocks). Relations of oolites at highest concentration localities, where they come in contact, is indifferent and carries no deformation traces. A similar picture is observed where oolites are in contact with exotic fragments.

Microscopic investigations of the ore determined sharp contacts of oolites and the cement, frequent external concentric shells of the cementing mass surrounding oolites, and cracks in oolites filled with the cement.

All these facts suggest that oolites were brought to the burial area in a consolidated state. Therefore, tobacco ores should be interpreted as a mechanical mix of solid elements (oolites and exotic fragments) and a colloid-gel cement. The lack of distinct layering in tobacco ore members is reliable evidence of uninterrupted sedimentation. Landslide structures and clayey portions are found in the ores. We will visualize the setting of stagnant oozy depressions which mechanically brought together diverse elements supplied by different routes. The enclosing cement could have been supplied as gel and colloid solutions; oolites were brought in by gravity flows from less deep generation provinces. Large exotic fragments (shells and pebbles) were delivered by currents during strong storms and sank to the bottom. Smaller shells and tree branches and trunks could have been brought by drift and sank.

A paucity of data on the mineral composition of ores is due to their susceptibility in change in conditions with access to free oxygen. The ore alterations have been described as connected with oxidative processes [2, 4, 5, 18]. The contact of specimens with the air was minimized during sampling and investigation. The specimens were preserved in an argon medium and sealed airtight to preserve the rock unaltered. Besides iron hydroxides, layer silicates are a major ore component [2, 4, 5, 7, 13, 18, 19]. A predominance of chloritic minerals in oolitic iron ores is generally assumed; this may be a result of a lack of crystallochemical data. In Kerch tobacco ores, a mix of silicon and aluminum hydrogels has been diagnosed previously [10, 15]; later, chamosite, lepto-chlorite, ferrichlorite, and hydroferrichlorite were diagnosed, emphasizing the specifics of Kerch chlorites [2, 4, 5, 7, 13, 18]; Fe-Al beidellite, an amorphous aluminosilicate material reminiscent of allophanoid and various mixed layer formations have been described as well [19].

A comprehensive study of the main ore components (oolites and cement) from the above-mentioned horizons was conducted with optical and state-of-the-art physical instruments for mineral investigation to determine the phase composition of the tobacco ores: a DRON-3 x-ray diffractometer (40 kV, 30 mA CuK_α), operated by E. V. Pokrovskaya, Geological Institute of the Academy of Sciences of the USSR (GIN); an ER-100 electronograph (100 kV, standard Al); a JEM-100C microscope with an energy dispersion analyzer (KEVEX-1500), operated by A. V. Mokhov, Institute of Mineral Resources [IMR], Academy of Sciences of the USSR; a UR-10 IR-spectrometer, operated by T. V. Dalmatov (GIN); a Cambridge-600 scanning microscope, operated by N. D. Serebrennikova (GIN); and a Camebax microprobe, operated by G. V. Karpova (GIN).

Results

Oolites and spherical segregates were investigated in specimens sampled from the rock and also in open polished sections. The study determined that these rock components have

TABLE 1. Chemical Determinations of Spherical Isolates of the First (specimens 1-4) and Second (specimens 5-8) Types from Lower Horizon of Tobacco Ore

Component	Specimen number							
	1	2	3	4	5	6	7	8
SiO ₂	33,943	37,385	37,850	36,380	6,587	7,487	4,937	4,228
Al ₂ O ₃	3,123	4,246	5,256	5,227	2,438	1,249	1,936	1,777
FeO	42,420	39,673	42,765	42,617	67,444	65,902	68,949	68,112
MnO	-	-	0,074	0,036	5,101	5,067	4,015	4,991
MgO	0,710	1,066	1,164	1,064	0,834	0,769	0,953	0,712
CaO	0,845	1,007	0,985	0,831	0,433	0,836	0,531	0,630
Na ₂ O	0,232	0,320	0,154	0,470	-	-	-	-
K ₂ O	0,518	0,217	0,238	0,277	0,322	0,068	0,105	0,163
P ₂ O ₅	0,482	0,070	0,069	0,183	0,976	1,138	0,860	1,711
Σ	82,274	84,267	88,632	87,148	84,135	82,515	82,287	82,324

Note. In this and subsequent tables, by way of convention, iron is given in ferrous form; the ratio of FeO and Fe₂O₃ was not determined.

different compositions and structures in different horizons. In the lower horizon the segregates appear as collomorphous clots: nonconcentric 0.2-0.5 mm spherules with an uneven and, as it were, "etched-out" surface. X-ray studies and microprobe investigation determined that they consist of early amorphous Fe-Si entities with presence of Al and minor amounts of other elements (Table 1, points 1-4). Another type of segregation is oval 0.2-0.5 mm forms with even edges. They are x-ray amorphous and are represented by Fe formations with Si, Mn, Al, and P impurities (see Table 1, points 5-8). Traces of hydrogoethite reflections are seen in x-ray patterns of all specimens.

There are several varieties of oolites from the top horizon: 1) round oolites with even distinct edges measuring from 0.1 to 0.5 mm; a concentric structure is unusual, although an outer shell may be present; 2) oolites with a collomorphous clot as a kernel, uneven edges, and an outer shell around the kernel, imparting a regular round shape to the oolite; and 3) oolites with a distinct concentric structure, up to 0.5 cm, with an irregular oval shape. According to x-ray electron diffractometric investigations, the oolites consist of amorphous matter, hydrogoethite, and a minor amount of tri- and dioctahedral Fe-containing smectite. The chemical compositions of the oolites are given in Table 2. Oolites of the third variety display an alternation of largely hydrogoethitic and essentially silicate (smectitic) concentric zones (points 5 and 6). No such differentiation is observed in oolites of the first and second groups (points 1-4). The phosphorus content is higher than in spherical segregates from the lower horizon (up to 3.7% P₂O₅). In fresh specimens, oolites are dark green; on contact with air they change color almost instantly. Initially, they may have consisted of allophanoids that contained ferrous and ferric iron, aluminum, phosphorus, and the minerals mentioned earlier.

By x-ray investigation and electron diffractometry the fractions of <0.001, 0.001-0.002, and 0.002-0.005 mm of the cement mass were investigated. The composition of fractions was virtually the same in all horizons. The cement from the lower horizon contained minor amounts of hydrogoethite and quartz and traces of di- and trioctahedral Fe-containing smectite; a high background indicated a substantial quantity of amorphous material. The cement of upper horizon oolites is multicomponent: amorphous matter, smectites, hydrogoethite, quartz, chlorite, and mica.

Smectites are a rock-forming mineral of tobacco ores. They remain virtually uninvestigated, although a detailed study would be of great interest. Smectite minerals are mostly associated with the cement of the top horizon of tobacco ores. Rapid oxidation makes it impossible to isolate cement in its natural condition; x-ray investigations studied smectite as a rock component. For electron diffractometric analysis, pieces of the oolite-cementing mass were sampled from unoxidized rock. Structural studies were also done on slowly oxidized ores in contact with atmospheric oxygen, which were oxidized rapidly by H₂O₂ treatment.

X-Ray Investigations. 1. Diffractograms of unoriented specimens of unoxidized rock (preserved in argon) in the low-angle region demonstrated a strong reflection with a spacing

TABLE 2. Chemical Determinations of Oolites from the Upper Horizon of Tobacco Ore

Component	Specimen number					
	1	2	3	4	5	6
SiO ₂	2,593	3,339	3,824	7,218	6,639	26,816
Al ₂ O ₃	0,979	1,604	1,351	4,626	2,587	7,158
FeO	73,276	68,890	73,431	60,974	64,035	33,151
MnO	0,411	0,279	0,363	0,387	1,418	0,301
MgO	0,365	0,324	0,294	0,407	0,627	1,580
CaO	0,558	0,600	0,712	0,673	0,772	0,901
K ₂ O	0,019	0,026	0,08	0,196	0,230	1,048
P ₂ O ₅	3,777	3,485	3,386	3,401	3,327	1,271
Σ	81,941	78,547	83,442	78,225	79,630	72,225

Note. Specimens 1-2) oolites of the first group; 3-4) oolites of the second group [3) middle oolites; 4) outer oolite shell]; 5-6) oolite of third group [5) substantially hydrogoethitic concentric form; 6) high-silicate substantially concentric form].

from 19 to 24 Å in various specimens. An ethyleneglycol treatment reduced the spacing to 16.8 Å. Similar diffraction patterns were observed for smectite minerals that contained organic complexes in interlayers [11]. Besides this reflection, diffractograms have reflections with d of 4.18 and 3.34 Å, representing hydrogoethite and quartz, and weak reflections with $d \sim 10$ Å, typical of micaceous minerals (Fig. 2A). There is also a slight presence of chloritic mineral. After 2-h heating at 500°C, the height of smectite packets was reduced to 10.1 Å; hydrogoethite was converted to hematite, identified from the reflection series with spacings 2.69, 2.51, 2.20, 1.84, and 1.69 Å. A high background in all diffraction curves was evidence of a substantial concentration of x-ray amorphous matter in the rock.

2. Rock oxidation in hydrogen peroxide is accompanied by a vigorous reaction. As a result of the process, the rock changes color from black-green to brown-yellow. Smectite reflection with $d \sim 15$ Å is seen on the diffractogram of the rock oxidized by hydrogen peroxide. After ethyleneglycol treatment, it is increased to 16.8 Å (see Fig. 2B). A similar picture is observed after day-long oxidation in the air.

The experiment showed that in natural conditions smectite mineral in the interlayers contains, in addition to exchange cations, organic matter, which is disintegrated by oxidation.

Natural oxidation of a rock kept for 2 weeks in open air at room temperature also resulted in a change of color from black-green to brown-cinnamon. The oxidized rock was divided into size fractions: 0.01-0.005, 0.005-0.002, 0.002-0.001, and <0.001 mm. An x-ray study of the fractions indicated that they had similar phase compositions. Smectite was the main mineral phase. Figure 2C presents diffractograms of oriented preparations of the fraction 0.005-0.002 [see Fig. 2C(I)] and <0.001 mm. In an air-dry specimen a reflection with a spacing of 14.7 Å is registered in the low-angle region. After the specimen is treated with ethyleneglycol it is increased to 16.8 Å; after 2-h annealing at 550°C the spacing shrinks to 10 Å. Like unoxidized rock, the fractions contain, besides the smectite mineral, quartz, hydrogoethite, and minor amounts of micaceous and chloritic minerals, as indicated on the diffractograms (see Fig. 2C). The considerable background in diffraction patterns indicated amorphous matter.

3. So as to determine the possibility of a transition of oxidized smectite from tobacco ores to the micaceous mineral, interlayer cations (Ca, Na, Mg) in the fraction of <0.001 mm were replaced by potassium cations by using the method described in [29]. The x-ray patterns of K-saturated smectite (fraction <0.001 mm, see Fig. 2D) display in the small-angle region a plateau and a distinct reflection typical for micaceous minerals with $d = 10.05$ Å. The second basal reflection is of an extremely low intensity, which is characteristic of high-Fe mica. After ethyleneglycol treatment the spacing of the first basal reflection was shifted to 9.85 Å. The shift represents some 15-20% of swelling interlayers in the micaceous mineral (hydromica) [9]. Besides the shift of the reflection (001) in mica after ethyleneglycol treatment, there is a considerable increase of the background in the small-angle re-

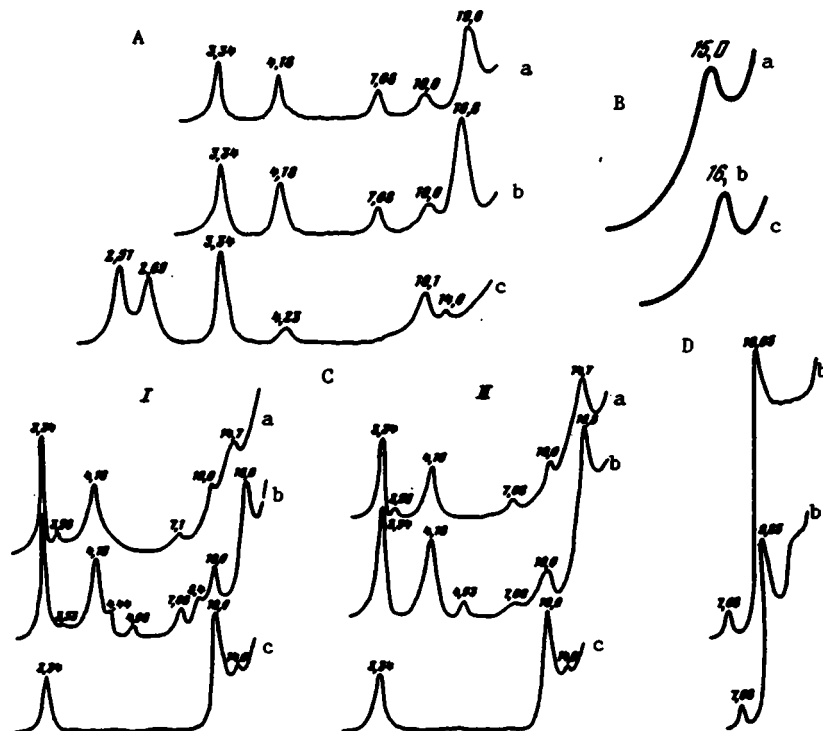


Fig. 2. Diffraction patterns: A) unoxidized rock; B) rock oxidized in H_2O_2 ; C) oriented preparation [I) fraction 0.002-0.005 mm; II) fraction <0.001 mm]; D) oriented preparation of K-treated smectite; a) natural specimen; b) treated with ethyleneglycol; c) heated at 550°C for 2 h.

gion, which a small bend near $\theta = 2.5^\circ$ (see Fig. 2D). The low-angle plateau on the diffractogram of K-saturated smectite and the high background are a product of the high degree of heterogeneity of the cation composition of interlayers in the smectite mineral that was not converted to mica by potassium treatment.

Electron Diffraction Investigation. 1. Specimens were prepared in water, blown through with argon to prevent oxidation. Electron diffraction patterns of oblique textures (EOT) of these specimens were typical for smectitic minerals: spatial reflections hkl were absent, while reflections $hk0$ were distinct, showing the absence of a three-dimensional ordering in the mineral structure. Ring electron diffraction patterns of smectites had two distinct reflections (060), and $d_1(060) = 1.54 \text{ \AA}$ and $d_2(060) = 1.51 \text{ \AA}$ (Fig. 3a); this corresponds to a unit cell parameter $b_1 = 9.24 \text{ \AA}$ and $b_0 = 0.06 \text{ \AA}$.

2. The EOT of oxidized smectites of all fractions (see above) were virtually the same as the EOT for unoxidized minerals. However, there was a drastic attenuation or a near disappearance of the reflection with $d_1(060) = 1.54 \text{ \AA}$, whereas the reflection with $d_2(060) = 1.51 \text{ \AA}$ remains clear and intense.

3. Electron diffraction studies of K-saturated smectites (fraction <0.001 mm) revealed three-dimensional reflections hkl in EOT with $k = 3n$ and with $k \neq 3n$ (see Fig. 3b). A drastic improvement of the diffraction pattern was obtained after 30 hydration-dehydration cycles of K-treated smectites (see Fig. 3c). These EOT exhibited a large set of distinct spatial reflections hkl . A geometric analysis of the positions of EOT reflections (see Fig. 3c) and an evaluation of their intensities determined the mineral's unit cell parameters ($a = 5.24$, $b = 9.07$, $c = 10.15 \text{ \AA}$, $\beta = 101.0^\circ$) and established that the diffraction pattern corresponds to high-iron micaceous mineral of 1M polytype modification, i.e., this K form of the oxidized smectite had a diffraction pattern reminiscent of a glauconitic mineral.

Electron Microscopic, Microdiffractational, and Microprobe Studies. The electron microscopic investigation of a specimen of the fraction <0.001 mm after potassium treatment showed it to consist of isometric (sometimes planklike) well aggregated grains, ranging in size from 0.05 to 1 μm . By microdiffractation and microprobe study, individual quartz and iron oxide

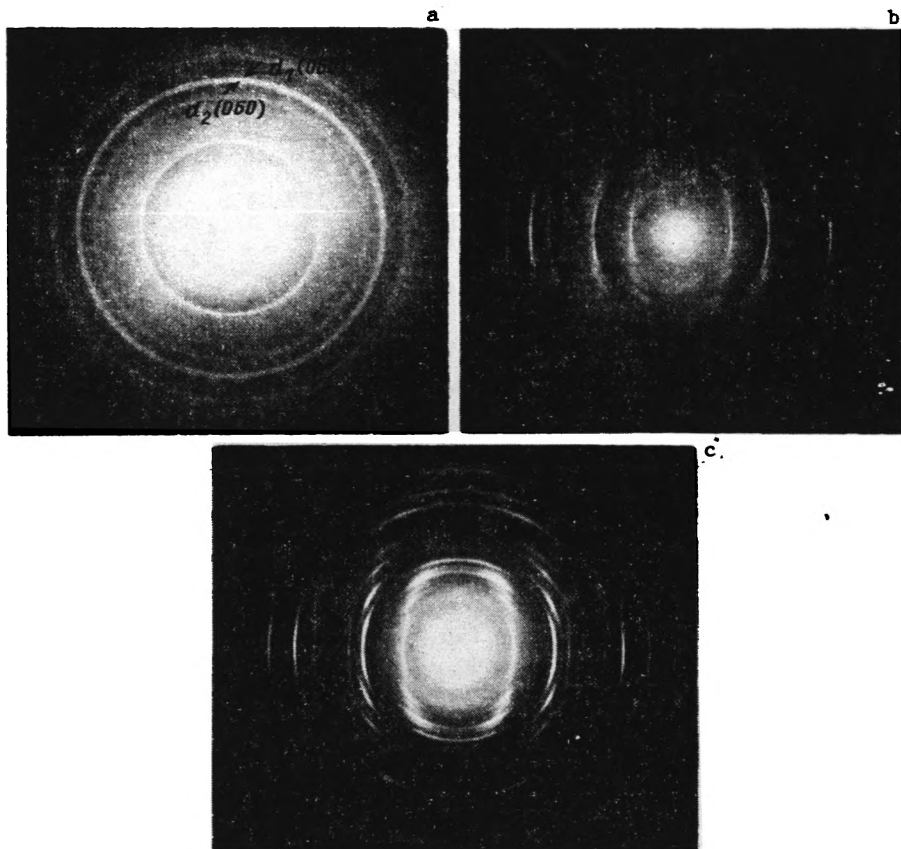


Fig. 3. Electron diffraction patterns: a) unoxidized smectite; b) K-saturated smectite; c) K-saturated smectite after 30 hydration-drying cycles.

grains could be easily diagnosed in the specimen, which had already been determined by the x-ray study.

All the grains containing layer silicates can be divided into two groups. The first (most widespread) group are grains consisting of a small number of textured lamellae (0.5-1 μm) of various orientations, producing point microdiffraction patterns (Fig. 4). The spacing $d(060)$ according to these electron diffraction patterns was 1.51-1.52 $\text{\AA}$. A quantitative energy dispersion analysis determined that the various portions of these grains are of a homogeneous composition (see Fig. 4). A quantitative microprobe study of the mineral identified the following contents, %: SiO_2 50, Fe_2O_3 25, K_2O 8, MgO 5, Al_2O_3 4, CaO 1, i.e., these grains belong to high-Fe layer silicates. The second group of grains includes aggregates made up of textured particles of various sizes (0.1-1 μm) disoriented in the lateral plane. The electron diffraction patterns of these grains are ring diffraction patterns (Fig. 5). The elemental composition of the grains is diverse. At the center of a grain, oxide contents are established, %: SiO_2 55, Fe_2O_3 25, Al_2O_3 7, MgO 5, K_2O 6, CaO 1, which is close to grains of the first group. At the edge of an aggregation, where very thin planklike lamellae are observed (see Fig. 5b), the following composition was determined, %: SiO_2 50, Al_2O_3 32, Fe_2O_3 5, MgO 2, K_2O 8, CaO 1. It may suggest a detrital mica (phengite-muscovite). A small amount of this mineral was diagnosed by x-ray study. Since some impurities may be present in the grains, the quantitative relations give only a general picture. A precise calculation of the crystallochemical formula is impossible.

Cation exchange in these specimens conducted in 1 N solution of K_2CO_3 produce large (2-3 mm across) and very thin, transparent, gel-like lamellae, opalescing in suspension. The lamellae were collected and dried. An x-ray investigation showed that they were x-ray amorphous. An analysis with a KEVEX-1500 microprobe determined a heterogeneous composition. Figure 6 presents energy dispersion spectra from various portions of a grain. We can identify silicic zones (see Fig. 6a) and ferruginous zones (see Fig. 6b), with minor amounts of Zn, Pb, Mg, Ca, and Si, or silicic-aluminum zones (see Fig. 6c). The grains apparently represent an amorphous gel obtained as an extract of the allophanoid specimen component.

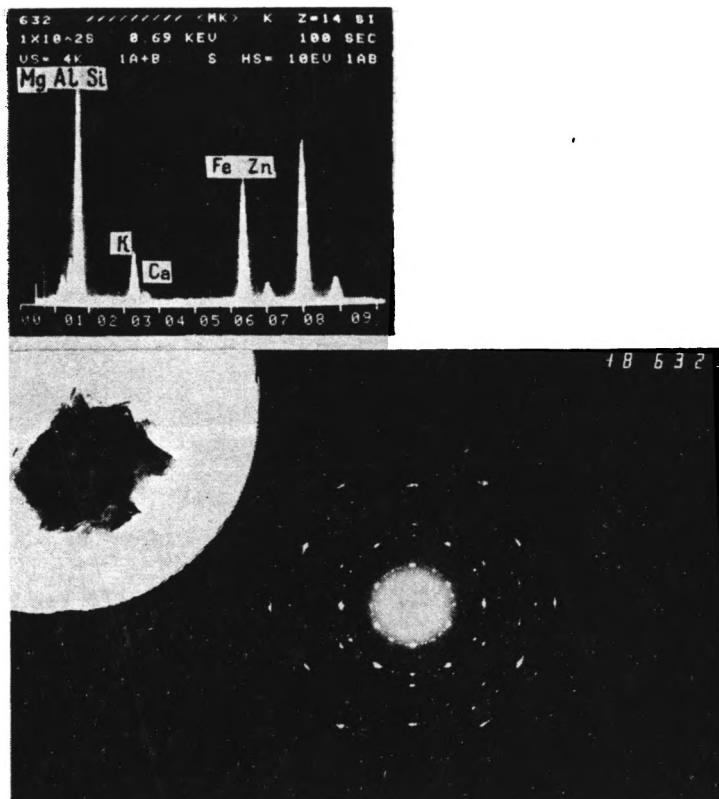


Fig. 4. Electron microscopic image, microdiffraction pattern, and energy dispersion spectra of the first group of layer silicate grains.

IR-Spectroscopic Study. The IR-spectra of oxidized smectites are similar to those of nontronite. In the region of valency oscillations of OH-groups, a broad absorption spectrum with a frequency of 3560 cm^{-1} was recorded (Fig. 7).

Scanning Microscopy. The cement of the tobacco ore consists of a considerable amount of iron oxides (Fig. 8a), appearing as cakelike aggregates from $1\text{ }\mu\text{m}$ to tens of microns. Cav- erns contain considerable quantities of well-contoured layer silicate leaflets (smectites). They form elaborate crystallization designs (see Fig. 8b), are attached to iron oxides (see Fig. 8c), or resemble the inner structure of glauconite globules (see Fig. 8d) [8].

In geomineralogical terms, tobacco ores can be said to be of a synthetic origin; they are sediments of relatively deep ooze depressions, where diverse components accumulated me- chanically: the cement was formed in situ; oolites were brought from outside, as were numer- ous exotic inclusions. This evolution left its imprint on the material and mineral composi- tion of oolites and cement which accounts for their different reactions of oxidation.

The study of smectite showed that in situ (unoxidized condition) its interlayers con- tain a considerable amount of organic matter, as well as Ca, Mg, and Na exchange cations. Diffraction studies (see above) indicated a decay of organic molecules in smectite inter- layers during oxidation. Organic matter can create a reducing setting and function as a buffer or "shield," protecting Fe^{2+} -ion oxidation in the smectite structure.

The electron diffraction study of the natural specimen determined that the smectite comprised two phases: trioctahedral ($b = 9.24\text{ }\text{\AA}$) and dioctahedral ($b = 9.06\text{ }\text{\AA}$) in equal pro- portions (see Fig. 6a). It is likely that the initial unoxidized state was one of triocta- hedral smectite, with a considerable amount of Fe^{2+} -cations in its octahedra. During speci- men preparation and study under a high-energy electron beam (100 kV) the mineral could have been partially oxidized with formation of dioctahedral Fe^{3+} -smectite. On the other hand, the two phases may coexist in situ. During oxidation the trioctahedral phase virtually dis- appears, and only dioctahedral Fe^{3+} -smectite with $b = 9.06\text{ }\text{\AA}$ is observed.

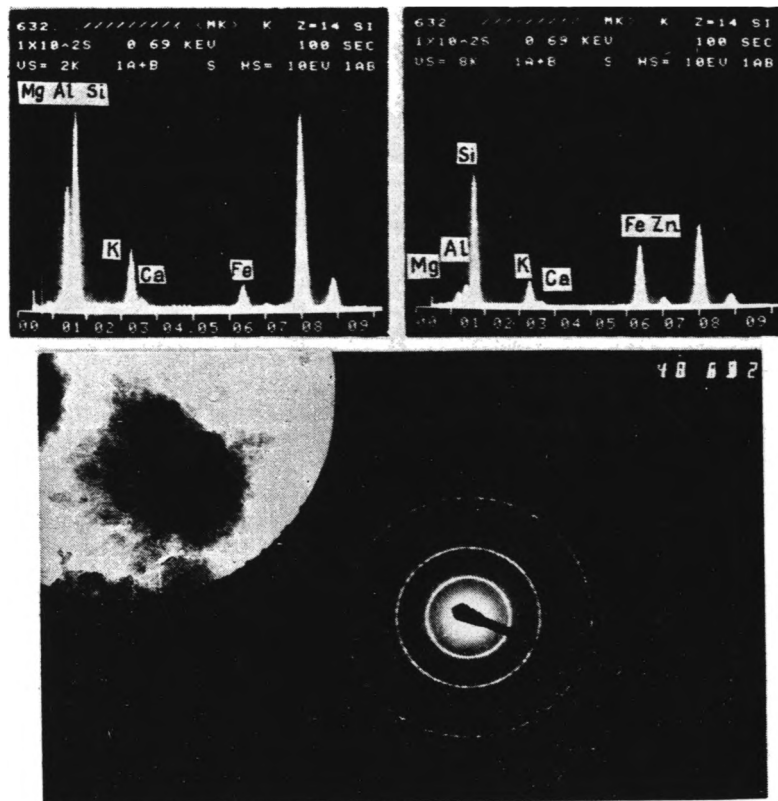


Fig. 5. Electron microscopic image and microdiffraction pattern of layer silicate of the second group; energy dispersion spectra [a) grain center; b) grain margin].

Up to now, there have been only two studies of Fe^{2+} -ion oxidation in trioctahedral smectite structures.

One of the studies [25] was concerned with Fe-smectite minerals from rhyolitic vitreous tuffs; it showed the minerals to consist of two phases: trioctahedral Fe-saponite ($b = 9.3 \text{ \AA}$) and dioctahedral Fe-Al smectite ($b = 9.06 \text{ \AA}$). NGR investigation determined that only Fe^{2+} -ions were present in the initial state in the structures of the two phases. Oxidation was a rapid process, changing mineral color from green to brown. According to NGR data, almost all Fe^{2+} -ions were converted to Fe^{3+} -ions. Iron oxidation did not significantly affect the mineral structure. The authors noted a reduction of the lateral dimension of 2:1 in both trioctahedral ($b = 9.22 \text{ \AA}$) and dioctahedral ($b = 9.01 \text{ \AA}$) smectites. Based on the experimental data [25], it was suggested that the excess positive charge produced by oxidation of iron ions in 2:1 smectite layers is compensated by a loss of protons from the hydroxy group. This is not accompanied by cation removal from the mineral structure, i.e., there is no additional octahedrization of Fe-saponite.

In [22], smectites from hydrothermal metalliferous Red Sea sediments were investigated. These minerals consist of trioctahedral varieties ($b = 9.3 \text{ \AA}$). NGR-spectroscopic studies of the initial specimens indicated Fe^{2+} - and Fe^{3+} -cations in the mineral structure. Oxidation was conducted for several hours; according to NGR data, like with Fe-saponites [25], almost all iron cations were oxidized to Fe^{3+} . Unlike oxidation of Fe-saponites, in this case iron cations were removed from the mineral structure. Sextuplets, typical for free iron oxides, appeared on NGR spectra. The end-product of oxidation of trioctahedral Fe^{2+} -smectite was a nontronitic mineral ($b = 9.09 \text{ \AA}$) [8]. The experimental data in [22] thus showed that oxidation of trioctahedral Fe-smectite resulted in dioctahedrization and retention of OH-group in the anion framework of its 2:1 layers.

A comparison of oxidation in Fe-containing trioctahedral smectites reveals a similarity in the mechanism of structural change of smectite from hydrothermal metalliferous Red Sea sediments [22] and the smectite from sedimentary formations. In both instances, there is a

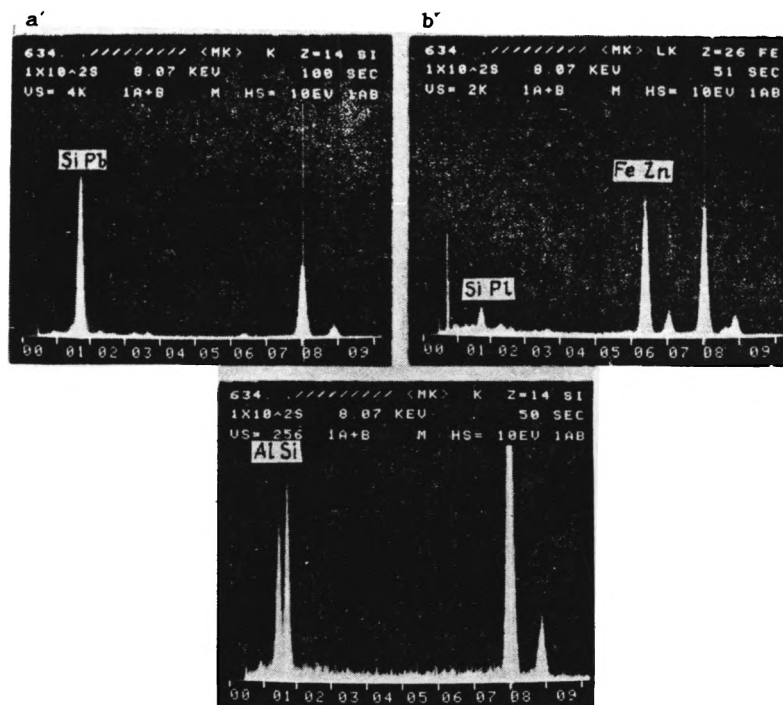


Fig. 6. Energy dispersion spectra of gellike lamellae.

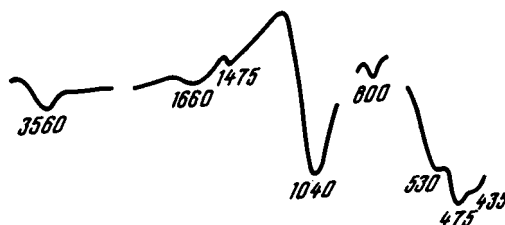


Fig. 7. IR-spectrum of oxidized smectite.

rapid transition from tri- to dioctahedral mineral. By contrast, oxidation of Fe-saponite from altered tuff [25] does not involve migration of octahedral cations from layer silicate structure. After oxidation the mineral remains trioctahedral, with a deprotonized anion framework. The differences in structural change during oxidation of trioctahedral Fe-smectites are presumably associated with the crystallochemical features of these minerals and their formation environments.

Studies of iron oxidation processes (Fe^{2+}) in Fe-containing minerals [25] suggested several possible mechanisms.

1. Reaction between Fe^{2+} -ion, the hydroxy group, and an additional oxygen in Fe^{2+} -chamosites [23] and amphiboles [20, 21].
2. Reaction between Fe^{2+} -ions and hydroxy groups with no additional oxygen, as in biotite [26, 27].
3. Oxidation of Fe^{2+} -ions with loss of interlayer cations [25].
4. Oxidation of Fe^{2+} -ions with loss of hydroxy group proton and its recovery, with subsequent irreversible removal of Fe^{3+} -ions from octahedral positions [24].
5. Oxidation of Fe^{2+} -ions at the expense of water molecules and removal of iron ions from mineral structure [22].

In principle, we cannot deny a partial deprotonization of 2:1 silicate layers in our case during intermediate mineral oxidation. However, the presence of OH-groups in oxidized smectite (see Fig. 7) is evidence that hydroxy group protons either did not participate in oxidation or were recovered after deprotonization (i.e., that oxidation evolved according

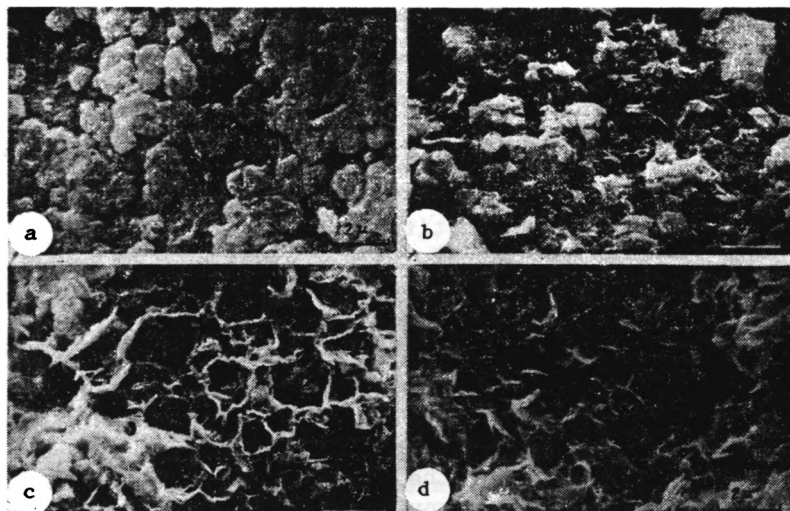
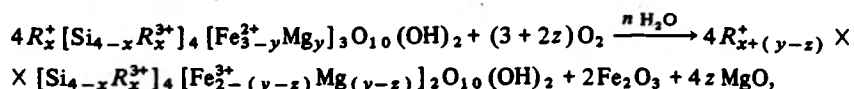


Fig. 8. Electron-microscopic image of cement portions.

to the scheme suggested in [24]). On the other hand, if an irretrievable loss of proton from the hydroxy group occurred during oxidation, the mineral remained trioctahedral, as was demonstrated in a study with oxidation of Fe-saponites [25].

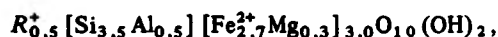
Oxidation of Fe^{2+} -ions in 2:1 smectite structure at the expense of water molecules, as suggested in [22], does not seem plausible to us. Oxidation obviously occurs with oxygen dissolved in water or extracted from the air. We investigated Fe^{2+} -containing smectite preserved for 3 months in argon-injected water. The mineral remained virtually unchanged as compared with its original state.

During oxidation the trioctahedral Fe^{2+} -containing smectite was converted to dioctahedral Fe^{3+} , containing variety which leads us to reconstruct this process. At the beginning of oxidation, organic matter in interlayers was destroyed with the aid of air oxygen. Then, some of the Fe^{2+} -ions in octahedra were oxidized to Fe^{3+} -ion, violating the charge equilibrium in the mineral structure. In order to retain equilibrium, the "excessive" R^{2+} octacations (Fe^{2+} , Mg), more mobile than Fe^{3+} -ions, migrated from the smectite structure, followed by oxidation of Fe^{2+} -ions. The process was completed when most Fe^{2+} -ions were oxidized and the steady state was achieved by the mineral. Oxidation of Fe^{2+} -smectite can be written as

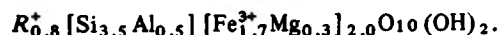


where x is the content of tetrahedral cations; y is the content of octahedral Mg cations; z is the loss of octahedral Mg cations during oxidation; and R^+ are hypothetical monovalent interlayer cations.

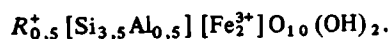
This reaction will be illustrated by an example. Assuming that the crystallochemical formula of trioctahedral Fe^{2+} -smectite is



we can say that the deficit of layer charge in the mineral is determined by the Si-for-Al substitution of trioctahedral cations, amounting to 0.5 f.u. If some of the iron ions (1 f.u.) migrate from the mineral structure during oxidation and Mg cations remain, the crystallochemical formula of oxidized dioctahedral Fe^{3+} -smectite will appear as



In that case, the tetrahedral charge (0.5 f.u.) is combined with octahedral charge (0.3 f.u.) and the charge deficit of the layer is increased to 0.8 f.u. If all Mg cations are removed together with Fe cations during oxidation, and the octahedra of 2:1 mineral layers contain no divalent cations, there is no increase of the layer charge, and the crystallochemical formula of oxidized dioctahedral smectite is



Microprobe investigations determined that Mg cations can be diagnosed in the structure of oxidized dioctahedral smectite after potassium treatment (see Fig. 4). Besides Mg, some of the unoxidized Fe^{2+} -ions may have remained in the structure. The potential presence of divalent octacations (Fe^{2+} , Mg) in dioctahedral 2:1 phyllosilicate obtained from trioctahedral varieties can increase the layer charge deficit as a result of oxidation. In this fashion, the transition of a smectite mineral to a micaceous mineral can be facilitated in a medium containing potassium cations that would be fixed irreversibly in interlayer positions. In our case, a large portion of oxidized smectite after potassium treatment was converted to a glauconitelike ferruginous micaceous mineral, with a small proportion of swelling packets. However, smectite minerals are also preserved with a considerable inhomogeneity of interlayer spacings. This can be due to various reasons: 1) an insufficient charge level and uneven charge distribution in the crystal volume; 2) the impossibility of replacing Fe^{3+} -cations that remain in interlayers of the mineral along with Ca, Na, and Mg cations and are not exchanged with potassium cations; and 3) a combination of these two factors.

In conclusion, we should note that Fe^{2+} -containing trioctahedral smectite has been discovered in sedimentary iron ore deposits for the first time. It exists due to the presence of organic matter, which creates a reductive environment and functions as a sort of buffer, shielding Fe^{2+} from oxidation. The existence of this smectite in tobacco ore was established by applying, for the first time, specimen conservation in argon after field sampling. Argon creates an inert medium and prevents the rock from oxidation. The nature of the organic matter, the forms in which it is found, and the causes of the reductive setting (for Fe^{2+}) in fossil condition are subjects for future study, but it is possible that these factors (as well as the presence of organics in the interlayer space of smectites) are associated with an influx of hydrocarbon gases, since the iron ore deposits are situated in an area of oil and gas shows and mud volcanos.

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INFLUENCE OF CATA- AND METAGENESIS ON REDISTRIBUTION OF MERCURY AND POLYMETALS IN SEDIMENTARY STRATA OF THE DONETS BASIN

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UDC 552.14:553.499(477.62)

The results of a study of impurity elements in various lithologic types of Donets Basin sedimentary rocks are reported. During postdiagenetic alteration (cata- and metagenesis) of the coal-bearing sedimentary strata, concentrations of ore impurity elements in sedimentary rocks - including mercury, lead, zinc, and copper - become redistributed. As a result, preconditions for development of commercial ore deposits are created.

The behavior of ore elements during sedimentation and postdiagenetic alterations (cata- and metagenesis) of sedimentary rocks and the related metal redistribution is an important aspect of regional geochemical studies which helps determine the regularities of formation and distribution of ore deposits not associated with magmatic activity. In areas where postdiagenetic rock alterations have been studied in detail and sedimentary strata have been classified stratigraphically on a well-elaborated scale allowing reliable tracing of horizons in plan, such investigations can be conducted quite effectively. The Donets Basin satisfies these requirements.

The Donets Basin is a metallogenic province [7]. The common commercial ore elements are mercury and polymetals. The patterns of deposit distribution and shows of these elements

Institute of Geological Sciences, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 74-84, 1989. Original article submitted October 6, 1987.

have been investigated by many authors and described in numerous publications [3]. However, the distribution of background values of these metals in the sedimentary beds, where they appear as impurities, has not been studied sufficiently.

There are two theories as to the source of metals in Donets ore deposits: one assumes that these are deep horizons of the earth's crust, i.e., that metals are of a juvenile origin [9, 11, 15]; the other theory [5, 10] holds that the bed enclosing coal-bearing rocks itself generated metalliferous solutions during cata- and metagenesis. The possibility of metal redistribution in the Carboniferous strata of the Donets Basin is of a practical as well as theoretical interest.

This study investigated the deposits of the Diamond Suite of the Middle Carboniferous in order to determine the distribution of mercury and polymetals in sedimentary beds of the Donets Basin and evaluate sedimentary rocks as a possible source of metals during cata- and metagenetic alterations.

Methods

The choice of the Diamond Suite as the object of research was due to the fact that it is widespread over the basin's area [4]. At the base it has four consistent lithologic horizons, traceable virtually everywhere: limestone L₁, argillite, siltstone, and sandstone, which form a coherent sedimentary cycle with a regular succession. The suite is found in zones with different groups of cata- and metagenesis and has been explored actively for coal, providing ample sampling opportunities for lithogeochemical studies.

Besides, the Diamond Suite contains no ore deposits and is virtually free of endogenous mineralization that could lead to a redistribution of primary metal concentrations.

Only cores from geologic exploration bore holes were taken for this study. Specimens from exposures were not used because of rock weathering and possible chemical alteration. Typically, a single sample of limestone and two or three samples from argillite, siltstone, and sandstone were extracted.

Since the stratigraphic sections of the coal-bearing Middle Carboniferous beds in the Donets Basin are well known, geologists often do not preserve cores from coal-free intervals and often do not take samples even during the course of drilling. The difficulty of sampling thus consisted in the fact that it was necessary to test sections immediately after drilling. When core samples are taken in field conditions, referencing errors may occur (approximately 1-3 m). To eliminate the possibility of accidental sampling of a wrong horizon, the sections of all the bore holes in an area were carefully correlated; the specimens were ultimately grouped according to lithologic horizons. Samples taken outside the respective horizons were disregarded.

Specimens weighed 0.2-1.0 kg, depending on the core diameter. They were ground to 200 mesh and subjected to a quantitative atom-absorption analysis for mercury (RAF-1 instrument with gold sorbents; sensitivity $1 \cdot 10^{-7}\%$). A semiquantitative spectral analysis of lead, zinc, and copper was also performed (sensitivity $1 \cdot 10^{-3}\%$). The statistical analysis of the data was performed on an ES1033 computer with an applications software package. Mean element concentrations in the samples were calculated under the assumptions of the two hypotheses - of normal and log-normal distribution. In addition, a massive determination of rocks in polished sections, chemical analysis, and x-ray structural studies of the fine fraction (0.01-0.001 mm) of terrigenous rocks were carried out.

In order to eliminate specimens with anomalous values from the samples, as recommended in [2], all individual specimens were tested with the following formula:

$$|A_i - \bar{A}| < v\sigma_{cm},$$

where A_i is the value of specimen from a sample; $\bar{A}$ is the arithmetic mean of the sample; σ_{cm} is the biased estimate of the variance of RMS; and v is a criterion borrowed from [2], for the confidence level of 95%.

As a result, we eliminated for the Starobel' section three specimens, for the mine 13-bis area two specimens, for Shakhterskii-Glubokii two specimens, and for Glubokii four specimens, which were apparently associated with microscopic accumulations of sulfides (pyrite and marcasite) that normally contain larger amounts of mercury.

TABLE 1

Location	Geologic-industrial coal-bearing district	Number of holes tested	Number of tests	Specimen sampling depth, m	Diamond Suite coal grade
Petrov	Starobel district	10	78	648-435	L (long flame)
13-bis mine field	Donetsk-Makeevka	8	103	835-697	LB (lean-baking)
Shakhterskii-Glubokii	Chistyakov-Snezhnyan	10	92	475-223	SA (semianthracite)
Fashchev-Nizhnii	Bokov-Khrustal'skii	5	65	930-628	A ₁ (anthracite)
Glubokii	Shakhtinsk-Nesvetaev	9	93	572-111	A ₂ (anthracite)

Note. Coal grades indicated according to [8].

Characteristics of the Area of Study

The samples were collected on five coal exploration sites (Table 1, Fig. 1) with different degrees of postdiagenetic rock alteration and coal metamorphism of the Diamond Suite. To eliminate samples with superimposed mineralization the sites were chosen at a distance from ore fields, arches of anticlinal folds, and large faults that favor migration of metaliferous fluids. Three locations were in depressions (see Fig. 1), one on a monocline, and one (mine 13-bis) close to a large French overthrust.

The locations studied encompassed an interval of coalification groups from long-flame coals (L) to anthracite (A₂). From 5 to 10 exploration bore holes were tested at each site. A total of 3 to 80 specific samples were collected for each horizon.

The compilation of stratification columns on the Diamond Suite for these locations (Fig. 2) determined that the four lithologic horizons are consistent to the strike and across the course of the region.

The rocks of the Petrov deposit, on the northern monoclinal slope of the Donets Basin, belong to the catagenetic stage with coals of grade L. The area was formed in platformal conditions and is different tectonically from other sites in the folded Donets Basin. Lithologic horizons vary in thickness from 2 to 5 m and are comparable.

The field of mine 13-bis is situated in the southeastern flank of the Kalmius-Torets depression. It is characterized by relatively thin clay rocks in the limestone roof and a thick sand horizon reaching 30 m and more.

The Shakhterskii-Glubokii section is located on the southern side of the Chistyakov-Snezhnyan depression. Coals belong to the SA grade. Argillite, siltstone, and sand horizons are of an approximately equal thickness (6-10 m).

The Fashchev-Nizhnii location is situated in the Bokov-Khrustalskaya depression between the main and northern Donets Basin anticlines. It has a relatively thick (up to 40 m) sand member and a smaller volume of clay layers. In all five holes drilled in this area there is no siltstone horizon; siltstone occurs directly on argillite (see Fig. 2).

Glubokii is located on the western centroclinal closure of limestone L₁ in the Shakhtinsk-Nesvetaev depression. It is characterized by the most advanced coal metamorphism (grade A₂). All the rocks are dark, almost gray, and very dense. All the horizons are thicker than in other locations; the section is, as it were, stretched.

Brief Petrographic Characteristics of Rocks

The limestone L₁ is of an organogenic detrital type; it consists of coarse and fine detritus, whole shells of various marine invertebrates (brachiopods, pelecypods, foraminifers, bryozoans, echinoderms, crinoids, etc.), and the cement binding them (microgranular calcite with a clay impurity). According to the degree of postdiagenetic alteration, the detrital and cementing materials have been recrystallized.

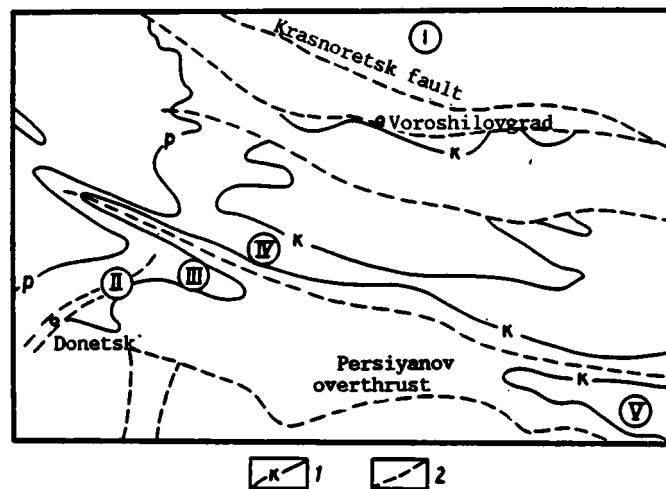


Fig. 1. Schematic geologic map of the Donets Basin:
1) marker horizons of Carboniferous limestone suites;
2) rupture faults; I-V) Diamond Suite testing sites
[I) Petrovskii, II) mine 13-bis area, III) Shakhterskii-Glubokii; IV) Fashchevskii-Nizhnii; V) Glubokii].

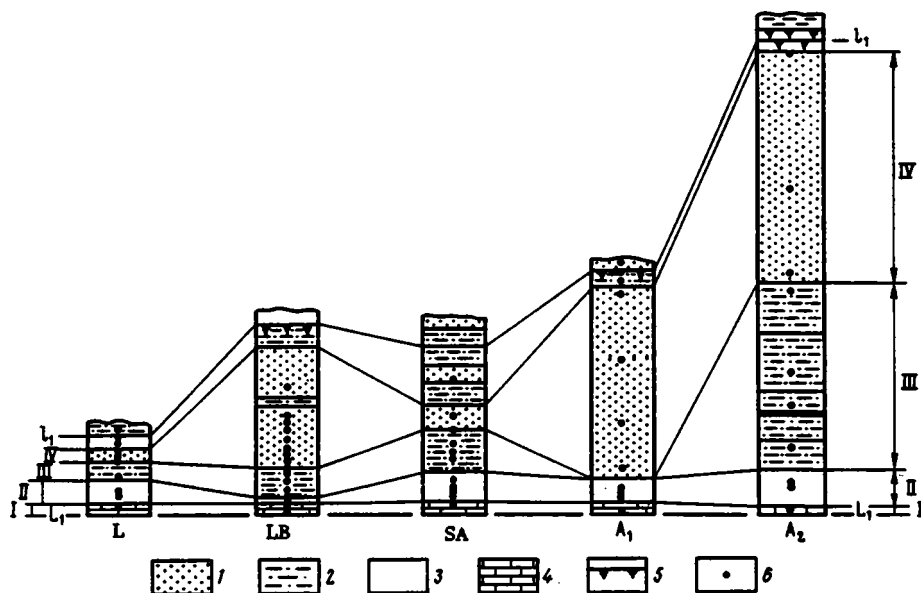


Fig. 2. Correlation of normal lithologic columns of Diamond Suite (C_2^6) in the interval between limestone L_1 and coaly seam l_1 : 1) sandstone; 2) siltstone; 3) argillite; 4) limestone; 5) coal seam; 6) sampling site. Lithologic horizons: I) limestone L_1 ; II) argillite; III) siltstone; IV) sandstone.

During the early catagenesis (coal grade L) the bulk (80-90%) of limestone consists of organic relict fragments and cementing microgranular, slightly recrystallized carbonates. Further structural change involved intense recrystallization that peaked at the time of formation of coal of the grade LB. Limestone is completely altered, with no features of primary textures and structures. The rock is small- and medium-grained, of a random structure. It is gray or light gray. The main rock-forming mineral is calcite, with a dolomite impurity.

At the advanced coal alteration stage (grades SA- A_1) limestone is represented by peli-tomorphic cryptocrystalline dark gray and black varieties. It has a mosaic texture, with cryptocrystalline relicts. The structure is homogeneous. The fauna in the rock is fully recrystallized; the contours of organic remains are rimmed by finely dispersed coaly formations. Mineralogically, the limestone consists of calcite and dolomite, with a minor side-

TABLE 2. Mercury Content in Rocks of the Diamond Suite, Donets Basin, $10^{-7}\%$

Rock (horizon)	Petrov deposit (L)				Mine 13-bis (LB)				Shakhtyrskii-Glubokii (SA)			
	n	$\bar{A}$	σ	V	n	$\bar{A}$	σ	V	n	$\bar{A}$	σ	V
Sandstone (IV)	9	44,2	22,1	0,49	82	34,3	12,0	0,29	12	36,5	11,8	0,32
Siltstone (III)	20	39,5	18,4	0,47	3	39,3	8,4	0,21	38	51,6	16,8	0,33
Argillite (II)	27	57,0	19,5	0,34	7	58,3	19,1	0,33	30	81,3	26,1	0,32
Terrigenous rocks (II, III, IV)	56	48,6			92	36,2			80	60,4		

Rock (horizon)	Fashchev-Nizhnii (A_1)				Glubokii (A_2)				Donets Basin (total)	
	n	$\bar{A}$	σ	V	n	$\bar{A}$	σ	V	n	$\bar{A}$
Sandstone (IV)	25	52,3	18,0	0,36	21	29,5	15,4	0,52	149	37,4
Siltstone (III)	-	-	-	-	34	46,8	22,0	0,47	95	46,9
Argillite (II)	23	69,6	24,0	0,34	16	75,8	26,7	0,35	103	69,8
Terrigenous rocks (II, III, IV)	48	60,5			71	48,2			347	49,7

Note. n) Number of samples; $\bar{A}$) arithmetic mean ($n \cdot 10^{-7}T$); σ) standard deviation; V) variation coefficient.

rite admixture. Terrigenous noncarbonate impurities are represented by clayey and coaly matter (up to 20%). The clay material is of a hydromicaceous-chloritic-sericitic composition.

In the occurrence area of ultraanthracites (coal grade A_2) the limestone bed consists of aphanitic cryptocrystalline calcareous argillites and argillitic limestone.

Depending on the proportion and granulometric size of detrital and clay material, terrigenous rocks in this interval are subdivided into argillites (clayey shales), siltstones (sand-clay shales), and sandstones. Argillites consist of a clay mass (75-90%) and clastic matter (10-25%); siltstone contains 60-75% of clastic and 25-40% of clay material. In the sandstones the proportions of clastic and clay material are 70-95 and 30-5%, respectively. Clastic matter in all rock varieties consists mainly of quartz, less often feldspar, and fragments of altered effusive rocks. Zircon, tourmaline, and sphene grains are the accessory minerals.

The composition of the clay phase varies depending on the degree of postdiagenetic alteration. At the stage where L-grade coal is formed, the main component of the clay phase is kaolinite, the dioctahedral mica, less chlorite, Fe-montmorillonite, and mixed-layer hydromicaceous-montmorillonitic formations. At the development phase of LB coal grade, the main component of the clay cement is dioctahedral hydromica, with some kaolinite, chlorite, and montmorillonite. The rock texture is pelitic, silt-pelitic, psammitic, and psammosiltic. Cement is basal, contact, contact-interstitial, or of attachment, indentation, or, sometimes, regeneration type.

During the formation stages of coals of grades SA- A_1A_2 , montmorillonite, kaolinite, and mixed-layer hydromica-montmorillonite virtually disappear from the clay component. The clay phase consists of dioctahedral hydromica (sericite) and chlorite. The texture is blastopelitic, blastosiltic, and microlepidoblastic. The cement is of contact-intersti-

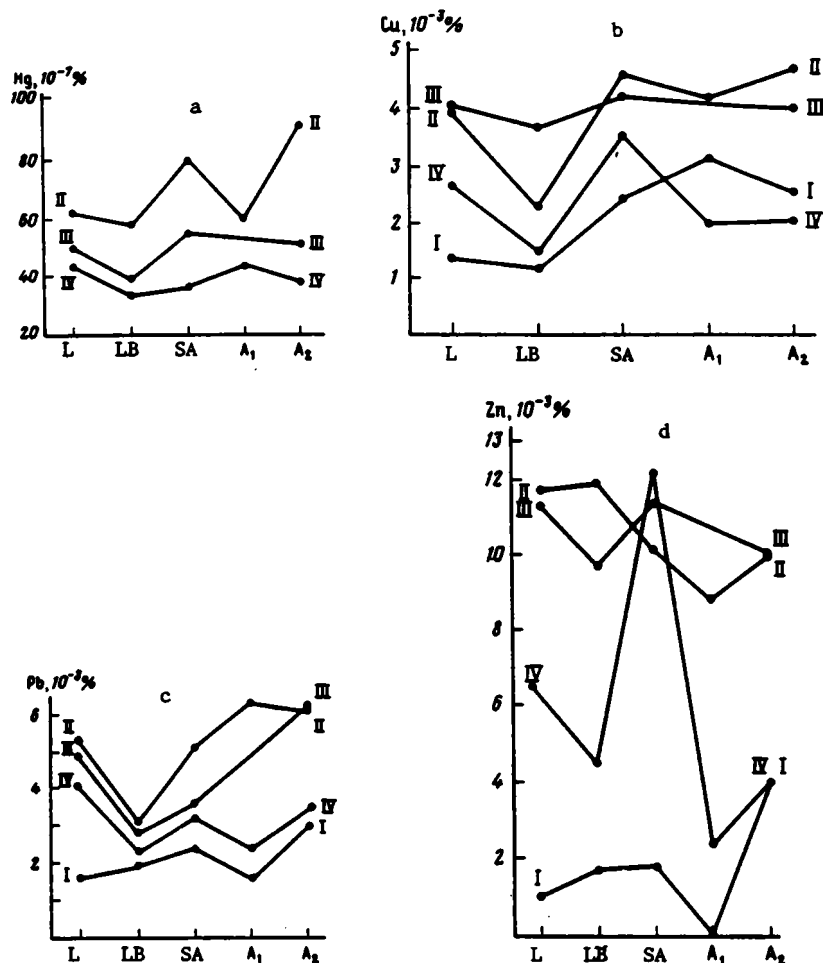


Fig. 3. Distribution of metals in Diamond Suite rocks: a) mercury; b) copper; c) lead; d) zinc. Rocks: I) limestone; II) argillite; III) siltstone; IV) sandstone.

tial, corrosional, and regenerative varieties. Secondary neomorphs, developed during metamorphism, are carbonates, represented by siderite and dolomite in all rock types.

Discussion of Results

We will first consider the distribution of metals according to lithologic rock varieties. The mean values for each rock type estimated for the entire territory of the Donets Basin (Table 2) show that the rocks have different metal concentrations. Mercury distribution in terrigenous rock indicates quite clearly that the rocks form a ranked series: sandstone → argillite → siltstone. The minimal values ($37.4 \cdot 10^{-7}\%$) are observed in sandstone; the maximum values ($69.8 \cdot 10^{-7}\%$) are observed in argillite, with intermediate values ($46.9 \cdot 10^{-7}\%$) in siltstone. Rocks are arranged in the same order according to lead, zinc, and copper (Fig. 3), i.e., concentration increases with increasing clay component. Zinc concentration in clay rocks (siltstone and argillite) is probably the only characteristic that remains constant.

Carbonate rocks (limestone L₁) contain relatively little metal. Lead, zinc, and copper values in them are lower than in terrigenous formations.* This distribution of mean metal concentrations is generally consistent with Strakhov's data [16] on predominant accumulation of lead, zinc, and copper in clay formations of the Donets Basin.

No detailed studies of mercury distribution in Donets Basin Carboniferous has been conducted previously; it is interesting to compare our data with existing information on the East European Platform [12]. The mean mercury contents ($39 \cdot 10^{-7}\%$) in sandstones virtually

*Data on mercury distribution in limestone are not reported here.

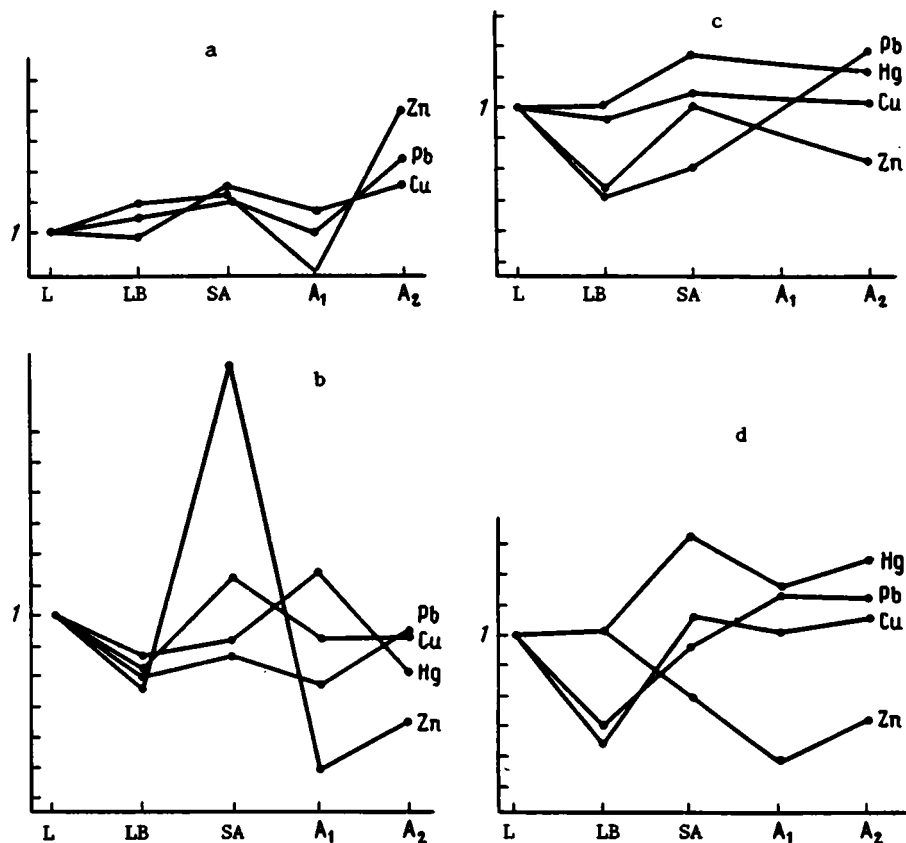


Fig. 4. Metal distribution in Diamond Suite rocks (relative to concentrations of formation stage of L grade coals): a) limestone; b) sandstone; c) siltstone; d) argillite.

coincide. As to the other lithologic varieties, the values for the Donets Basin are higher: for siltstones by 20%, for argillite by 200%, and for limestone by 70% [6] (see Table 2). Unlike the East European Platform and the East Kamchatka synclinorium [12], the Donets Basin has a preference for mercury accumulation in clay sediments. This is observed not only in the rocks at the center of the basin, which had evolved through more advanced catagenetic stages, but also in relatively less cemented bodies of the Petrov deposit, on the southern slope of the Voronezh anticlines, i.e., similar to platforms in sedimentation conditions.

The fact that the values for sandstones coincide seems to indicate that the sensitivity of analysis was similar in both instances. The discrepancy of data on other rocks may suggest a different behavior of metals during accumulation of sediments in the East European Platform and the Donets Basin. Clay rocks of the Donets Basin are extremely rich in organics, which, according to Ozerova and Aidin'yan [13], is an active mercury concentrator. In the East European Platform clay and argillite probably did not have a comparable amount of organic material.

We will now discuss the differences in metal concentrations in rocks of individual locations, i.e., the effect of the degree of postdiagenetic alteration. Figure 3 plots concentrations as a function of degree of cata- and metagenesis. The degree of alteration is expressed by industrial coal grades found in the respective intervals of the Diamond Suite.

Mercury. Terrigenous rocks are characterized by a regular pattern: generally, concentrations rise to a maximum and then decline. Argillites and siltstones have the highest values during the formation stage of SA coals; for sandstones the maximum is shifted toward the grade A_1 .

Copper. Limestone and terrigenous rocks have largely similar copper concentrations (see Fig. 3b). All rocks have a minimum during LB coal formation, then a maximum at SA coal, and then a slight decline (from 3.5 to 2 percentage points) in the anthracite zone, especially clear in sandstones.

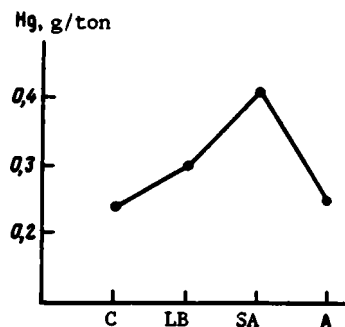


Fig. 5. Mercury distribution in Eastern Donets Basin coals as a function of degree of metamorphism [1]. Coal grades: C) coking; LB) lean-baking; SA) semianthracite; A) anthracite.

Lead. According to lead concentrations, the rocks form an increasing ranked series: limestone → sandstone → siltstone → argillite (see Fig. 3c). The extreme members of this series behave differently during progressive cata- and metagenesis. Argillite and siltstone have a minimum at the time of formation of LB coal; they then rise rapidly to a maximum at stages A_1 and A_2 . The limestone curve has no minimum at the stage of LB coal formation. The values grow almost linearly; only for A_1 there is a local drop of metal content. Sandstone, which occupies the intermediate position in the series, has both minima: at coal grades LB and A_1 .

Zinc. The rocks are subdivided into three groups according to zinc concentrations (see Fig. 3d): argillite and siltstone have the highest zinc values; limestone has the lowest concentration, with sandstone occupying the intermediate position. The zinc distribution in limestone is virtually identical to that of lead: a slow growth with a minimum during formation of coal grade A_1 . By contrast, terrigenous rocks are different. With increasing cata- and metagenesis the proportion of metal in argillite and sandstone is rapidly decreased; the process is less clear in siltstone. Against the background of general decline, minimal values are recorded during the formation stages of coal grades LB and A_1 . There is a local maximum in the stage of SA coal formation. For sandstone the maximum is so high that it even exceeds the values of the clay rocks. High zinc concentrations have been observed in all 10 bore holes of this location, i.e., they are not accidental.

We will also discuss variations of metal contents for each lithologic variety during the course of cata- and metagenetic alteration.

Limestone. Metal contents in limestone increase in proportion to cata- and metagenetic rock alteration. The distribution of elements is characterized by a local minimum during formation of A_1 coals. The minimum is deepest for zinc: the content drops beneath the sensitivity threshold. This means that with progressive cata- and metagenesis of the sedimentary bed limestone concentrates metals (Fig. 4a).

Sandstone. Metal content variation curves for sandstone are quite similar and differ only in amplitude (see Fig. 4b). In the interval of coal grades LB there is a decrease of values, followed by a rise at SA (where zinc and copper reach the maximum), there is a decline during stage A_1 , followed by a slight rise for A_2 . The maximum for mercury falls on A_1 ; it then declines rapidly to an absolute minimum. Unlike limestone, where the element concentrations increase, sandstone is characterized by a general decrease of metal concentrations from the initial level (coal grade L). This level is exceeded only at the peak point of the curves.

Siltstone. Mercury, copper, and zinc distributions in siltstone are similar to sandstone curves: There is a decline of values, followed by a maximum during formation of SA coals, and then a decrease. The behavior of lead is different. After a minimum at the LB stage, contents rise without declining and reach a maximum at the A_2 stage. Estimating the extreme points of the interval (L and A_2), we should note that zinc is the only metal whose content declined relative to the initial level; copper content remained the same, while mercury and lead concentrations increased (see Fig. 4c).

Siltstone and sandstone fix the local maximum of metal contents during formation of SA grade coals. The general zinc concentration decreases, that of copper remains at the original level, while mercury and lead contents are increased.

Argillite. Lead and copper curves for argillite are similar (see Fig. 4d): A decrease during formation of LB coals, then a growth to a maximum, which is retained through several

stages. Copper reaches a maximum at the SA stage; lead at stage A₁; mercury and zinc behave differently. Until the formation of LB coals, their contents remain constant; the concentration of zinc then declines to a minimum at the SA stage. In the interval A₁-A₂ zinc and mercury concentrations rise but never reach the maximum values.

Discussion

The preceding description suggests that limestone exhibits the clearest picture of metal distribution. All metal contents increase with advancing postdiagenetic rock alteration. The locations studied (see Fig. 1) are distributed unevenly over the basin, so that a regular growth of concentrations (see Fig. 4) cannot be attributed to any primary synsedimentary distribution of elements in the sediment. The rise of metal concentration with advancing postdiagenetic alteration of limestone should presumably be attributed to increased sorptive and reactive capacities of calcium carbonate for metals. The property of carbonate rocks as mercury concentrators was first established by Saukov [14]. Other metals may be adsorbed by a similar mechanism. With increasing temperature and pressure during cata- and metagenesis, limestone capacity for interaction with metals should be enhanced.

Terrigenous rocks exhibit a more complex distribution than limestones. Disregarding minor details, we can say that the general metal concentration in sandstones is lowered, remaining largely at a constant level in siltstones, and is increased in argillites. Limestone, which closes this series, has a pronounced tendency for metal accumulation.

Against the general trend described for each rock, there is this specific feature: metal concentration increases with attainment of the maximum during formation of SA-grade coal, followed by a decline during the development toward anthracites. There are exceptions to this pattern (lead in siltstone, lead and zinc in argillite), but it appears to be a general regularity with a curve approaching log-normal distribution. An independent study of toxic metals in coals as a function of coal seam metamorphism conducted in Rostov Province of the Donets Basin [1] revealed a similar regularity. Concentrations of elements grow until formation of SA coals, and then decrease toward anthracites (Fig. 5). Semianthracite rocks have other specific features, including mineralogic similarities. In particular, these and similar rocks of the lean-coal stage (Le) are also characterized by a decrease in the clay fraction of terrigenous rocks of the concentration of minerals such as montmorillonite, kaolinite, mixed-layer hydromica-montmorillonite, and an increase of dioctahedral hydromica (sericite) and chlorite. Another characteristic features is development of quartz veinlets.

We believe that this indicates a jumplike change of the physicochemical condition of sedimentary rocks at the stage of formation of Le-SA coal grades: a restructuring of clay minerals, improved quartz solubility, enhanced circulation of fluids, and redistribution of metals. All these processes manifested themselves intensely in the development zone of anthracites. For certain rocks (such as sandstones) these developments could release a portion of the metals from the mineral and carry them by fluids to higher zones, enriching the semianthracite zone. These released metals may have formed commercial ore placers. By contrast, other (clayey and carbonate) rocks exhibit a tendency for metal concentration.

The following conclusions have been drawn from this study:

1. There is a predominant accumulation of metals (mercury, lead, zinc, and copper) in clay varieties of the Diamond Suite of the Donets Basin during sedimentogenesis.
2. Postdiagenetic rock alteration involved a change of metal concentration. The pattern of change was controlled by the lithologic type and the metal itself. With advancing cata- and metagenetic alteration, metal content in sandstones generally declined. In siltstone it fluctuated, remaining at nearly a constant level; in argillite it increased slightly; in limestones the concentration growth was the strongest.
3. The advancing postdiagenetic rock alteration was initially accompanied by a rise of metal concentration with rock, reaching a maximum during the time of formation of SA grade coal; it then declined toward anthracites. Mobilization of metals from rocks in the anthracite stage, most obvious in sand formations, created preconditions for development of commercial deposits.

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SECONDARY ALTERATIONS OF SALINE ROCKS IN THE UPPER KAMSK DEPOSIT

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UDC 533.632:552.14

In the article, we establish for the first time a series of stages for the post-sedimentary alterations of halopelitic material occurring in rock salt. We show that there are tectonic faults in the supra-saline deposits which are probably surrounded by pre-contact zones of microhypergenically altered saline rocks. The precontact zones are exploration cues for the presence of tectonic dislocations.

This report concerns patterns of post-sedimentary alteration of halopelitic material present in rock salt in a salt-marl stratum of the Upper Kamsk. Halogenic deposits undergo various alterations after sedimentation. Among the first such alterations are processes of recrystallization and collective crystallization which can manifest immediately following sedimentation and continue through periods of diagenesis-catagenesis-hypergenesis. Unfortunately, the petrographic-mineralogical data frequently does not allow one to confidently delineate the dia- and catagenetic stages in the alteration of halogenic deposits, and, in the majority of cases, authors have assigned such stages to the general category of post-sedimentary alterations occurring in saline rocks.

Hypergene processes are most definitively and clearly manifest in halogenic rocks. However, the scales and results of their activity depend upon the intensities of the processes involved. We investigated the initial phase of hypergenesis, when leaching of chloride salts has still not occurred and, therefore, the salt beds themselves are preserved and desulfidization of the halopelitic material is not complete. This phenomenon has been found in the lower portion of the zone of hypergenesis (retrograde diagenesis). The secondary alterations of the rocks are negligible in scale, but they are of significant genetic and practical interest and can be distinguished in the earliest, initial phase of microhypergenesis. When distinguishing processes of microhypergenesis in halogenic rocks, we attributed approximately the same content to the rocks as did Vassoevich [1, 2] in the concept of cryptohypergenesis within sedimentary rocks. In our version of microhypergene transformations based upon the data of mineralogical-petrographic and geochemical investigations, we depart from considering the very close paragenesis of the halite of the rock salt and the halopelitic material occurring with it. The latter, in turn, is represented as a complex combination of authigenic (sulfate-carbonate) and terrigenous (predominately silicate aluminosilicate) components which, in cases when they are at all involved in even the most negligible manifestations of microhypergenesis, initiate a series of natural alterations in halogenic rocks.

The results from our investigations, which we have presented below, reflect an attempt by the authors over many years to investigate the saline rocks of both the upper Upper Kamsk deposit and the halogenic deposits of Eastern Siberia and Pricaspia, and the Starobinsk deposit [13]. The following stages in the manifestation of post-sedimentary micro-hypergene processes can be distinguished: 1) unmanifest (or almost unmanifest); 2) initial (weakly manifest); 3) distinct (manifest); 4) mature. The stages differ from one another with respect to the intensity of the transformation of the rocks and have the following characteristics.

1. During the unmanifest (almost unmanifest) stage of postsedimentary alterations, the halopelitic components in the saline rock and sulfate-marl beds maintain the specific features of their sedimentation almost completely. Their structure is pelitomorphous (for grain sizes less than or approximately 0.001 mm). Microstructure is either entirely unmanifest or shows microlayering with interlayer thicknesses of approximately 0.01-0.10 mm. The microlayers are either indistinguishable with respect to color or recognizable by various tints

*Deceased.

Uralkalii Planning Section, Berezniki. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 85-92, March-April, 1989. Original article submitted December 15, 1987.

ranging from grey to black. The lighter (grey) tones are usually associated with a predominance of pelitomorphic carbonate deposits. The darker tones (dark-greys, blacks) are associated with pelitomorphic anhydrites, in part calcareous, and also siliceous and aluminosiliceous.

2. The initial (weakly manifest) stage is characterized by processes of collective crystallization of components of the halopelitic material. Anhydrite formations of phacoidal, nodular, and lumplike micro- and very fine-grained structure occur primarily at contacts of the halopelitic material with halite grains. The results of the very earliest hypergene hydration of nodular anhydrite occlusions can manifest during the initial stage. Gypsum neoformations possessing only mineralogical significance arise at the peripheries of the nodules.

The collective crystallization of the carbonate portion of the pelitomorphic material also results in a certain isolation of the sites of such material, although the nodules are still not as distinct as in nodular anhydrite. The dimensions of the grains and crystals of carbonates within such sites can often reach 0.01-0.10 mm. At these sizes, they are easily identified by the immersion method.

The first signs of alterations of the silicate and aluminosilicate components of the halopelitic material appear simultaneous. This is expressed in the formation of the finest micro-sintered opal (which is difficult to identify) and in the peculiarities associated with the diversity structured chalcedony, sometimes transitional to chalcedony-quartz rosettes and other forms of neoformations. However, this early "silicate hypergenesis" of the initial stage is only of genetic interest in connection with the small scale of its manifestations and its indistinct "inconclusive manifestations" which are difficult to pick out on microphotographs.

3. The distinct (manifest) stage is characterized by a significant isolation of the products of early-hypergene activity. Collective crystallization and recrystallization of anhydrite begins within the composition of the halopelitic material at a number of sites. The early crystalline formations of anhydrite usually appear with grains and crystals from 0.01 to 0.1-0.2 mm in size; this is particularly the case at their boundary with halite regions. The recrystallization of the anhydrite and its nodular formations continues, especially at their peripheral regions, where finely prismatic and acicular coroniform fringes of anhydrite sometimes appear. In cases where early-hypergene hydration of the anhydrite proceeds, every possible combination of neogenetic gypsum and preserved (also predominant in the sulfate portion) anhydrite are formed. In such cases, microinclusions of relict anhydrite can usually be detected in the gypsumized areas. Collective crystallization of the carbonate components, often leading to the appearance of individual or numerous clustered rhombohedral crystals or irregular forms of dolomite (or calcite) grains up to 0.3-mm in size, also takes place, predominantly along contacts of the halopelitic material and the halite of the rock salt enclosing it.

Further breakdown of the terrigenous components of the halopelitic material takes place during the distinct stage of early hypergenesis. Sinters associated with early "silicate hypergenesis" (variously positioned, many-faceted combinations of chalcedony and quartz) appear in greater or less quantity. They can easily be located on photomicrographs, even at small magnifications.

4. The mature stage of early hypergenesis in halopelitic deposits is accompanied most importantly by significant hydration of anhydrite and the appearance of gypsum in the midst of the anhydrite. Gypsum plays the role of the principal silicate component in the halopelitic portion of the rock. The gypsumization of the anhydrite is an "open door" to a procession of complex and multifaceted processes involving the salinization of the halopelitic environment to one degree or another. First of all, the pelitomorphic dolomite present in the composition of the halopelitic portion and possessing a huge surface associate with its fine crystals becomes an unstable component at contacts with neogenetic gypsum. It enters into an interaction with the gypsum along the reversible path of a natural Haidinger reaction leading to the formation of calcite ($\text{CaCO}_3 \cdot \text{MgCO}_3 + \text{CaSO}_4 \rightarrow \text{CaCO}_3 + \text{MgSO}_4$).* The terrigenous material undergoing decomposition isolates significant quantities of silica within a number of its components. The silica, together with magnesium liberated from the dolomite during the process of its calcitization, yields chlorite, illite, and surplus silica in the form of a mass of authigenic chalcedony-quartz minerals associated with neoformations which

*Actual paragenesis of calcite and gypsum are cited [5].

TABLE 1. Development of Processes of Microhypergenesis in the Salt-Bearing Portion of the Section of the Saline-Marl Stratum of the Upper Kamsk Deposit (mine BKRU-2, mine shaft 3)

Depth, minerals	Number of rhythm pack- et; terri- genous (A) and saline (B) portions	Rocks and their positions in the section	Thick- ness, m	Stages in processes of micro- hypergenesis				Macro- hyper- genesis
				Almost unmani- fest	Initial weakly manifest	Dis- tinctly manifest	Distinct mature	
272.8	4-9	Non-saline deposits of the saline-marl stratum	84.0					+
		Second layer of rock salt and its halopelites	1.0				+	
		Second layer of sulfate-marl rock	0.7				+	
	B	First layer of rock salt and its halopelites	2.1				+	
		First layer of sulfate-marl rock	2.0				+	
	3	Third bed of rock salt and its halopelites	4.9				+	
289.0	A	Third bed of sulfate-marl rock	5.5				+	
		Halopelites from the second bed of rock salt	12.9		+			
	2	Second bed of rock salt			+			
303.3	A	Second bed of sulfate-marl rock	1.4	+				
	B	Halopelites from the first bed of rock salt	6.5	+				
	1	First bed of rock salt		+				
310.9	A	First bed of sulfate-marl rock	1.1	+				
321.4	Incrusted rock salt	Rock salt	10.6	+				

can overcrowd the halopelitic regions of the rock during the mature stage of early hypergenesis. This surplus silica can either distribute itself randomly in the halopelitic regions or form traces of indistinctly expressed post-sedimentary interlayers in the rocks. Numerous examples of the various stages associated with microhypergenesis are presented in an atlas [13].

In the Upper Kamsk deposit, features associated with manifestations of the four stages of microhypergenesis can be traced in the alterations of saline deposits along the third shaft of the Second Bereznikov Potash Plant. A petrographic description of these deposits was given by Melkov [5]. Along the shaft section, the saline rocks of the stratum lie in the interval from the first to the third rhythm packet inclusively (Table 1). Above, lie terrigenous nonsaline deposits with a total thickness of 84 m. Their characterization corresponds to that of a composite nonsaline type of section associated with the salt-marl stratum [11].

An analysis of the data indicates (see Table 1) that noticeable post-sedimentary alterations do not occur in the deposits of salt crust and in the lower portion of the salt-marl stratum. The analysis also shows that the chief features associated with the original sedimentation of these deposits is preserved. The initial stage of the microhypergene processes can be found in a bed of rock salt within the second rhythm packet. Here, collective crystallization of anhydrite, with the formation of its finely fractured forms, is widespread. In a bed of sulfate-marl rocks in the third rhythm packet, a paragenesis of calcite with gypsum occurs. This is probably an indication of partial dedolomitization of pelitomorphous dolomite with the formation of calcite. However, the major portion of the calcite is of a sedimentary pelitomorphous variety. This paragenesis with a partial manifestation of chalcidization and quartzification of the halopelitic material indicates the stage of distinct manifestation of secondary processes. The top portion of the section of the third rhythm packet, possessing a thickness of 10.7 m, corresponds to the mature stage of development. Extremely graphic and intense secondary alterations appear at the basal bed of the rock salt. In this bed, the hydration of anhydrite is accompanied not only by intense chalcidization and quartzification, but also by calcification of halite grains and areas of fine-grained anhydrite. Compact silicification develops locally in small (1-3 mm) halopelitic regions: The chalcedony of these regions has a yellowish-brown color and usually a parallel-filamentous structure in microsections. Sometimes, quartz and carbonate crystals grow into the halite during decomposition of the halopelitic material within such regions [13]. An analogous situation with respect to the microhypergenetic decomposition of halopelites can be detected in the thin layers of rock salt within the third rhythm packet. Besides the hydration products of anhydrite and silification of the halopelitic material here, the appearance of intermediate- and coarsely crystalline calcite is noticeable as a product of the dedolomitization of pelitomorphous dolomite (or, possibly, as a product of post-sedimentary collective recrystallization of primary pelitomorphous calcite). The processes associated with formation of calcite resulting from dedolomitization in hypergenetically altered halogenic-carbonate strata have been characterized in detail in [7], although, unfortunately without the needed connection with the phenomena of silification, which play an extremely important role in our material.

The process of hypergenetic alteration of rock intensified somewhat above the third rhythm packet. Complete leaching of the rock salt from the halogenic deposits took place [8] and karst cavities with lengths of several meters and heights of 10-20 cm were formed at the "terrigenous deposits-rock salt" contact [3]. In the neighboring second shaft, an accumulation of secondary mirabilites and halite was noted in one of the karst cavities. The ratios present (g/liter) were: Na_2SO_4 88.30; NaCl 121.77; CaSO_4 2.21; MgSO_4 0.69; Br 0.034. Consequently, the data presented above indicates that a precontact zone of microhypergenetically transformed rocks 10-m in thickness exists in the saline deposits near their transition boundary to terrigenous-chemogenic deposits. The presence of such a transitional zone allows it to be used (under the appropriate conditions) for predicting the location of the very birthplace of weakly mineralized waters, since the intensity of secondary alterations in the rocks increases in the direction of the water source.

At the Upper Kamsk potash deposit, water supply to the saline strata is realized by two routes: under the influence of the injection of beds of saline rocks into a zone of active interchange during folding, as took place in the previous example, or as a result of water infiltration to the saline strata along tectonically weakened zones. In the first

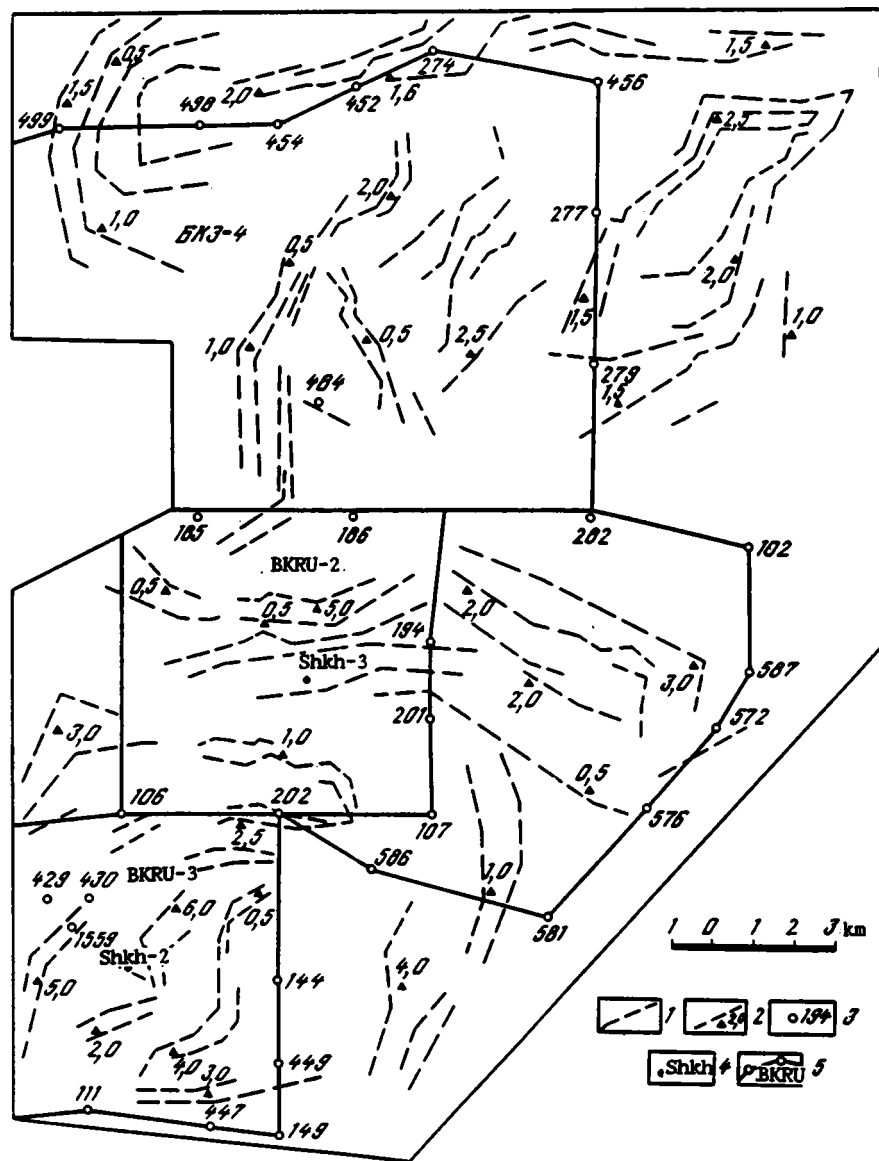


Fig. 1. Diagram of the distribution of tectonically weakened zones in the southern portion of the Upper Kamsk potash deposit. 1) Tectonically weakened zones; 2) vertical shift of tectonic blocks, m; 3) drill hole and its number; 4) Shakhtie shaft and its number; 5) contours of mine field.

case, regional leaching of the rock salt takes place at anticlines associated with tectonic upheavals [3, 4, 12] or at the border areas of the deposit [6]. The second path of arrival for water has still been insufficiently investigated, but it has great practical significance, since tectonic dislocations breaking the top horizons of the saline deposits guide the water directly to the potash deposit by disrupting the water-resistant soil over the commercially valuable beds. Tectonically weakened zones were discovered in 1979 by Yu. A. Tret'yakov using a geomorphological method based upon a morphometric analysis of the water drainage in the southern portion of the locality (Fig. 1). The theoretical basis for the method [9, 10] is the idea that vertical tectonic movements of the crystalline basement and the sedimentary mantle are widely reflected in the structure of river profiles. For example, selective (linear) scouring river beds takes place at outcrops of fault breaks at the surface. Areas of steeper (abnormal) slope appear on the river's extended profile. The faults which we discovered are the youngest in age (neotectonic). They are low-amplitude according to the amplitude of shift of the blocks (primarily increases in elevation amounting to 1-6 m). The dip angles of the plane of the fault breaks is steep (70-90°), since the faults formed under the influence of radially directly tectonic forces. In plan view, these faults

form circular structures several kilometers in diameter or occur in the form of series of parallel faults up to 6 km long.

The attempt to exploit the Upper Kamsk deposit showed that tectonic stresses were reflected, as a rule, in the form of plastic (fold) deformations and that stress unloading took place in the form of rupturing deformations in the suprasaline rocks. The boundary of the transition from fault breaks to folds continues approximately along the roof of the incrustated rock salt and reflects the dependence of the type of deformation upon the physico-mechanical properties of the rocks. Along the stratigraphic section from the surface to the roof of the rock salt, including the saline-marl stratum, tectonically weakened zones are sites of intense fissuring of saline and terrigenous rocks with the presence of microfaults with amplitudes of up to 0.4 m. When the fissured zones are penetrated by boreholes, the rock fragments are additionally abraided in the drilling pipe and assume the forms of the well rounded formations which were previously and erroneously classified as gravellites of Ural rocks. According to the data of G. M. Konovalov, which was gathered while studying similar formations during the progress of the second shaft at mine BKRU-3, the gravelly grains are marl, rock salt, anhydrite, quartz, and pyrite. Rounded fragments of marl and rock salt with sizes from 1 to 8 cm are frequently encountered. The quantity of coarsely fragmented and clayey material constitutes approximately 50% of the volume.

The tectonically weakened zones are unevenly supplied with water. This is connected with the nonidentical expansions of fissures in different directions. For example, the fault breaks most supplied with water in the BK3-4 and BKRU-3 mine fields have meridional and northeastern strikes, respectively. It is quite probable in these cases that precontact zones of microhypergenetically transformed rocks also exist around the tectonic fault breaks in the salt-bearing deposits, but they are oriented subvertically. Thus, discovery of zones of precontact alterations in halogenic rocks permits a more precise prediction of the location of the fault break itself.

1. A zone of microhypergenetically altered rocks more than 10-m thick occurs in beds of rock salt at the contact with flooded terrigenous deposits. The secondary alterations affect only the halopelitic material of the rock salt, material in which various manifestations of anhydrite hydration, quartzification of terrigenous material, and alteration of the composition of carbonates can be detected. Four stages in the post-sedimentary transformation of halopelitic material can be distinguished on the basis of the intensity of the microhypergene process.

2. The continuity of the suprasaline deposits is interrupted by tectonic breaks. The breaks have steep dip angles and are distributed along the section within an interval from the surface to the horizon associated with the roof of the rock salt. The fault breaks serve as primary paths for the migration of water to the potash deposit. The existence of broad precontact zones of microhypergenetically altered rocks is probable around the tectonic faults in the saline deposits. This should be taken into consideration when predicting or searching for the location of the fault break itself.

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LITHOLOGY, FACIES COMPOSITION, AND ACCUMULATION CONDITIONS OF THE MOST RECENT DEPOSITS ON THE SEYCHELLES ISLANDS

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UDC 551.35(265/265)

Three basic types of sections, characterized by upland islands, uplifted reefs, and low accumulative islands, are distinguished among the most recent deposits of the exposed Seychelles Islands. The genetic relations of the deposits represent subaerial (elluvial, slope, eolian), subaquatic and aquatic (reef, lagoonal, marine), and biogenic (guano, phosphorite) formations. These comprise the facies and facies series.

The Seychelles Islands, which lie in the equatorial part of the Indian Ocean, represent a wide archipelago of islands, varying in origin, relief, and rock composition. The greatest part of the island land is made up of a cover of most recent deposits with varying lithology and genesis. Three basic types of section are distinguished.

The first type characterizes the upland islands (Mahe, Praslin, Silhouette, etc.). Its characteristics are: 1) the general presence of an original sequence of parent rocks, which are Paleozoic granites; 2) a relatively wide genetic range of deposits, with clear predominance of sediments with subaerial genesis: elluvial, landslide, and particularly elluvial-landslide; 3) terrigenous rocks dominate the material composition of the deposits, that is, the products of the destruction of parental granites. Marine carbonate formations are only developed on the periphery of islands.

The second type of section is peculiar to islands which represent uplifted reefs (Saint Pierre, Aldabra, Assumption). It has a two part structure. The lower, larger part of the structure is made up of shallow water limestones of the uplifted reef, while the smaller, accumulative part is represented by young aquatic and subaerial formations. Signs of prolonged interruption of marine sediment accumulation are universally traced between the deposits of the reef platform and the accumulative cover.

Moscow State University. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 93-105, March-April, 1989. Original article submitted April 27, 1987.

The third type of section is mostly distributed on the lower accumulative islands which lie on the edge of the Seychelles bank, that is, the Amirante Islands and particularly the islands of the Farquhar group. It is characterized by an extremely uniform and simple structure (thin young accumulative formations of principally coastal marine genesis).

Finally, it is also possible to distinguish an intermediate type of section, close to the second, with the only difference that in the visible part of the section, the thickness of the limestones of the uplifted reef and the accumulative cover are close. It is similar in several peculiarities of structure to features of the third type of structure. This first of all seems of cover distribution on islands of coastal-marine sediments, that is not distinguished for islands with second type of structure of section. The intermediate type is characteristic for islands with weakly uplifted reefs (Farquhar, Astov, Kosmoledo).

The following genetic varieties are distinguished among the various sediments of island land of the Seychelles Islands: subaerial (elluvial, slope, eolian), subaquatic and aquatic (fluvial, biogenic, lagoonal, and marine). They are composed from a series of facies (Table 1).

Elluvial formations (subaerial deposits, laterite facies) are in particular represented by a red weathering crust. The soil cover on the granites of the upland islands is generally expressed in the form of a deeply developed laterite type soil profile. On the atolls, the soil profile develops weakly, in the form of skeletal carbonate soils, with only weak traces of soil formation in the surface layer of sediments. The position of the islands in the islands in the equatorial zone with high temperatures, abundant sediments, and thick plant life predetermined the active development of biological processes, causing intense weathering of the parental granites and their transformation into typical laterites. Elluvium is widely developed on the flattened tops or outlying slopes of the granitic massif of the upland islands. The composition of the deposits may be quite diverse depending on the time of formation, preservation, geomorphological position, and the degree and depth of working of the granites. On the whole, the following structural features are typical for the laterite section. In the upper part it is strongly weathered, approaching soil forming rocks of sandy loam composition, of yellow and brown-orange color. The complete absence of sorting in the sand fraction, expressed on the histograms and the "sawtoothed" curve of mechanical composition (Fig. 1) is characteristic of them. Quartz sharply predominates (>75%) in the sand fraction. Strongly weathered grains of feldspars, partially leached and replaced by kaolinite minerals, are present in lesser quantities. The heavy fraction is saturated by authigenic minerals, iron hydroxides, generally illmenite and hematite. Lower in the section the deposits acquire a "denser" red-brown and brick-crimson color, becoming argillaceous, with sharper differentiation of mechanical composition. Kaolinite and gibbsite with an admixture of goethite predominate among the clay minerals, based on data of x-ray structural analysis. Based on material of thermal analysis, the composition of the crust is kaolinite-goethite. At the base of the deposits the quantity of coarse grained material again increases, that is, gravels of corroded quartz, and there is a gradual transition to strongly weathered parental rock. On the whole, in the formation of elluvium there is a transformation of the feldspars and hornblende from the crustal granites into kaolinite, and even into gibbsite, and quartz enrichment of the weathering crust. If we exclude predominating spallithic composition, products of alluvium are composed of Al_2O_3 (60.7%), Fe_2O_3 (9.6%), and H_2O (29.8%).

Among slope sediments we detect: landslide-talus (gravitational), elluvial-gravitational, and talus.

Landslide (gravitational) accumulations are developed episodically along vertical and steep slopes of mountain massifs. In composition this is varied-block material of granites, filled in by finer rock fragments.

Specific elluvial-gravitational formations are mostly distributed among the most recent deposits of the upland islands. They represent ancient landslide accumulations strongly reworked by weathering processes. Two varieties are distinguished among them: 1) a coarsely detrital and varied blocky variety, composed from fragments of granites of various size and preservation, and 2) a relatively fine variety, displaying matrix material. The matrix essentially represents a friable, variously weathered material of originally granitic composition, close to the weathering crusts, but less reworked, with traces of small displacements in section. These are pulverized red-brown and brown-yellow sandy loams and sands, with mechanical composition similar to laterites, of principally quartzose and quartz-feldspar composition. The wide development of elluvial-gravitational deposits among the upland

TABLE 1. Facies of Most Recent Deposits and Their Distribution

Genetic classification				Characteristic lithologic features	Distribution		
Group	Type	Sub-Type	Facies		Upland islands	Atolls	
						Uplifted	Low
Subaerial	Elluvial	Weathering crusts	Laterites	Red rock of aluminum-iron-silicate composition	Wide	Insignificant	--
	Slope		Elluvial-gravitational (facies of ancient landslide)	Strongly weathered material of varied thickness in friable red matrix	"	--	--
			Landslide (gravitational)	Various detrital, principally lumpy accumulations	"	--	--
			Talus	Weakly sorted sandy loam-sandstone	Moderate	--	--
	Eolian		Eolian	Well sorted fine-grained sands, forming dunes and hills	--	Wide*	Insignificant
Subaerial-Subaquatic	Biogenic (connected with guano)		Island phosphorites	Phosphorite containing rocks of brown and light brown color	--	"	Moderate
Aquatic and sub-aquatic	Fluvial		Flood plains	Sandy loam-mud deposits with plant remnants, humic	Insignificant	--	--
			Channel	Various detrital material of granitic composition in sandy quartz and quartz-feldspar matrix	"	--	--
	Lagoonal		Mangroves	Sand-mud deposits with mass plant remnants	Moderate	--	--
			Intraisland lagoons	Well sorted fine carbonate sands with plant material	--	Moderate	--
			Atoll lagoons	Variously sorted carbonate sands	--	Wide	Wide

TABLE 1 (continued)

Genetic classification				Characteristic lithologic features	Distribution		
Group	Type	Sub-Type	Facies		Upland islands	Atolls	
						Uplifted	Low
	Marine	Coastal-marine	?	Sands with fragments of organogenic material	Moderate	Moderate	Wide
			Modern and ancient beach and terrace	Sorted sands and sandstones (beach-rock)	"	"	"
		Shallow water marine	Island sands of reef	Well sorted sands and channel sands	--	Insignificant	"
				Dense light limestones, partially recrystallized	Insignificant	Wide	--

*In zone of southeast tradewind.

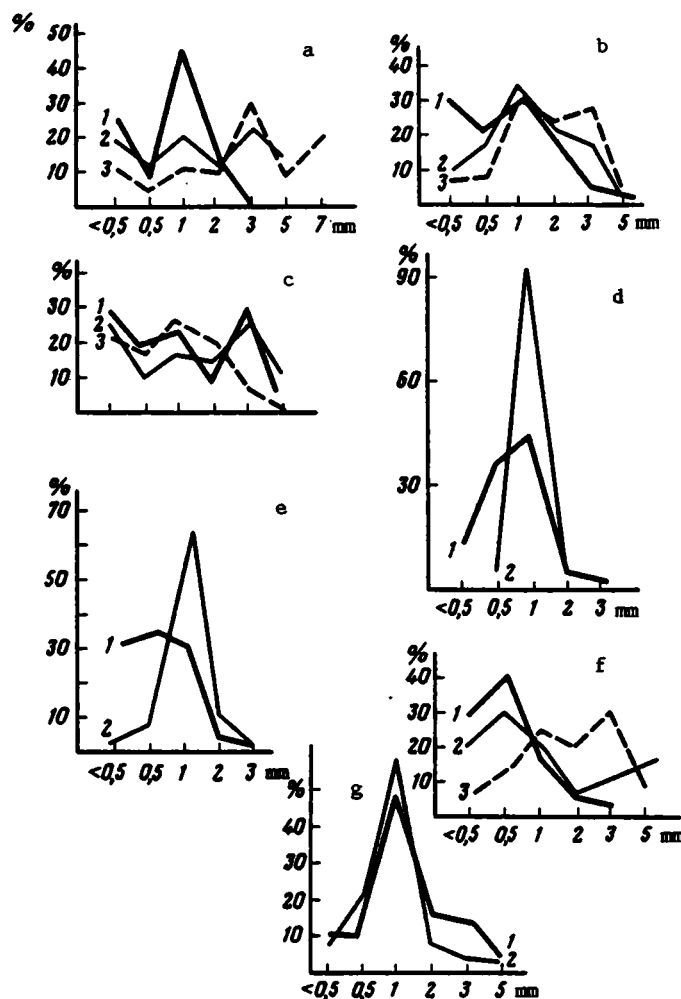


Fig. 1. Curve characters of indexes of granulometric composition from various genetic types of the most recent deposits from Mahe Island. a) Weathering crust; b) alluvial-gravitational; c) talus; d) coastal-marine (beach); e) coastal-marine (terrace); f) lagoonal; g) alluvial; 1-3) sample numbers.

islands of the Seychelles bank is caused by peculiarities of their relief: the presence of granitic massifs, which guarantees constant slope collapse by joint fractures, and their position in the equatorial climate, with the intense processes of crustal rock destruction into friable laterites. The last member of the slope genetic series, talus deposits, is of limited development on the islands. The cause of this includes slope blocking by landslide and elluvial-gravitational formations and thick plant cover. The noted portion of talus deposits in the slope structure is only observed on mildly sloping areas which are utilized by man for agricultural and structural needs, that is, everywhere where vegetation and the blocky "carcass" of the slopes are liquidated.

The composition of talus deposits is close to material of the filler in the adjacent elluvial-gravitational formations. It is distinguished from them by the presence of a weakly weathered layered texture caused by interlayered distribution of coarsely detrital material in the sequence. These are sandy loam to sandy, weakly sorted or practically unsorted deposits of yellow-brown color, of small thickness. A noted differentiation of mineral material, expressed by increased content of the heavy fraction (Table 2), particularly owing to the concentration of magnetic minerals, is established in the talus in comparison with weathering crust and elluvial-gravitational deposits.

Eolian sediments, representing typical subaerial formations, are characteristic for islands positioned in the zone of southeast tradewinds. They are most widely developed on windward shores of islands, where they form individual hills, dunes, and dune systems ex-

tended along the coast. Sands from drying areas, beaches, and breaker zones serve as sources of eolian sediments supply. The coarsest sand accumulations, which form dunes up to 15 m or more, are correlated to places of wide drying and steep parts of bays, where beach rock is absent or strongly destroyed. Thus, disregarding the width and extent of the windward coasts of islands positioned on path of southeast tradewinds, eolian deposits are actively formed only in places where large drying fields of coastal-marine sediments are present. The eolian sands are close in composition to sediments of their supply areas, and they are distinguished by a finer mechanical composition, better sorting (see Fig. 1), and the presence of a stain on the sandstones.

With respect to facies, the varied subaquatic-aquatic group of deposits is composed in particular from marine sediments; the other genetic varieties are less developed in the sections of the most recent deposits of island land. They are first of all related to alluvial formations, which are characteristic only for the relatively large upland islands, where they are developed in weakly reworked valleys of intermittent and permanent water flows. In the upper and middle parts of the valleys this is principally a recent channel facies of alluvium-coarsely detrital material in a heterogeneous sand matrix of principally quartzic and quartz-feldspar composition. On the narrow near-marine plain, where the valleys are best developed, deposits of this facies are noted lying above parts of sections which are also called terrace. An increase is established in the alluvium (up to 9%) in the yield of the heavy and particularly the magnetic fraction (see Table 2), and a high content of stable minerals, such as illmenite and zircon and particularly hornblende (up to 20% and more). The composition of this sediment facies is relatively fine, clearly layered, with elements of cyclicity. A relatively coarse, variably sorted (see Fig. 1) sand composition with predominance of quartz and quartz-feldspar components in the light fraction and presence of numerous coarsely detrital material is characteristic of the alluvium of the whole. All of the microelements recorded in the weathering crust are noted in the alluvium of Mahe Island (Table 3), but in decreased concentrations. Only some increase is noted in Ni, Zn, and Co, with a sharp increase in the admixture of strontium, with a tendency to its still more significant increase in marine sediments.

Alluvial deposits in river mouths generally emerge into lagoons; forming with them sediments of a single paragenetic series. Deposits of this type of lagoon, in the same way as the similar alluvial formations, are generally made up of varied grained sands with poorly sorted, principally quartz composition, with some quantity of coarsely detrital, variably rounded carbonate material, which enters the lagoon from the sea in time of storm.

Facies of swamps, intra-island lagoons, and atoll lagoons are distinguished among the lagoonal deposits of the islands. Sediments of mangrove swamps are developed on the coasts of upland islands and on the peripheries of several atoll lagoons (Kosmoledo, Aldabra). They have a relatively fine sand-mud composition and contain a large quantity of plant material in various stages of decomposition with a rotten odor. Various authigenic (calcite, iron hydroxides, and marcasite) and accessory (pyroxenes, sphene, epidote, and others) minerals are detected along with the general mineral composition of sediments in the mangrove lagoon deposits on Mahe Island.

In facies of the intra-island atoll lagoons, revealed on dry land and beaches, the sands contain a varied admixture of coarsely detrital material, with poorer rounding than on the adjacent marine portions of the coasts.

The facies of coastal-marine and shallow marine formations are distributed among the aquatic deposits of the islands, which are predominantly of atoll sediment types. Coastal-marine deposits are represented by rocks from the accumulative terrace cover, plates of beach rock, and modern sediments of beach and land.

Terrace deposits are developed on the periphery of the upland islands and in parts of uplifted atolls (Aldabra, Assumption, Farquahar, Providence). They are absent on the lower islands, where single-aged sands and sandstones make up the island land. In genetic relations, these are sediments of ancient beaches with a system of coastal banks lithified to varying degree, at the present time brought out from under wave action and forming a terracelike surface up to 3 m high. These sands are friable and at ground water level variably grained in composition, generally fine and medium grain sized, and exclusively carbonate on the atolls. On the coasts of the upland islands the deposits are more varied in composition; quartz-carbonate and quartz-feldspar-carbonate form the light fraction; a high content of illmenite, sometimes to 13%, is noted in the heavy fraction (see Table 2).

TABLE 2. Mineral Composition of Mahe Island (compiled by L. I. Bazilevskaya)

Genesis	Yield of heavy fraction, %	Mineral composition (0.25-0.1 mm fraction), %								
		heavy fraction					light fraction			
		ilmenite	zircon	hornblende	iron hydroxide	concretions	quartz	feldspar	coral fragments	shell fragments
Elluvial	2,4	6,8	-	0,5	92,5	-	+	+	-	-
Elluvial-landslide	0,1	70,0	1,7	1,1	27,0	-	+	+	-	-
"	3,8	97,2	0,6	-	0,6	1,7	+	+	-	-
Talus	4,1	73,4	0,7	2,8	18,4	4,2	+	+	-	-
Alluvial	9,0	70,3	1,5	22,2	5,2	0,7	+	+	-	-
"	4,4	47,0	2,0	19,0	30,0	2,0	+	+	-	-
Marine (terrace)	13,3	91,5	0,5	3,4	2,9	1,4	+	+	+	+
Marine (beach)	-	-	-	-	-	-	+	-	+	+

Note. The "plus" sign denotes the presence of the mineral, the "minus" denotes its absence.

TABLE 3. Strontium Content in Carbonate Rocks, 10⁻³%

Sample Number	Occurrence	Uplifted reef-flat	Beach
1	Aldabra atoll (South Island)	30	500
2	The same	8	500
3	The same (Polimni Island)	20	500
4	Assumption Island	80	500
5	Astov Island	80	400

Rocks of beach rock which occur practically over all of the Seychelles Islands are relatively ancient beach formations. As a rule, they are represented by several plates of sandstone, comprising variably aged generations of rock. They are of carbonate, less often quartz-carbonate (on the upland islands) rock composition, grey and light-grey, variably grained, composed from fragments of corals, sometimes significantly foraminiferal, with inclusions of sponge spicules, bryozoans, and chalcid algae. A beach type of banded texture is characteristic. On shores with strong wave action, rocks of beach rock are often represented by gravellites and conglomerates. The rock cement is always carbonate. The presence of low and high magnesian calcite and acicular aragonite is noted in the cement. Various processes undoubtedly participating in the process of beach rock cementation are: capillary evaporation of sea water, degassing of ground waters, and mixing of fresh and sea waters in the beach zone. Formation of beach rock was accomplished under the following conditions: 1) the wide development of carbonate sands on beaches; 2) the presence of constant high temperature in the oceanic waters and air; 3) the great quantity of atmospheric sediments; 4) the position of the deposits in high and low tide zone. A necessary prerequisite was also apparently that the state of the input-outgo balance of beach alluvia was close to dynamic equilibrium. In the opposite case, for a deficit of alluvium, the beach will erode and recede, and beach rock will not successfully form. For a positive balance of alluvia, cementation of sands also will not be successful due to the process of beach accretion.

Contemporary coastal marine formations are sediments of beach and land, widely distributed along the island marine shores. In composition these are carbonate sands, grey and light grey, generally fine and medium grained, well sorted (see Fig. 1), seldom coarse grained, containing various fragmental, variously rounded material. The composition of beach deposits are principally of carbonate formations. Only a few beaches of upland islands (Mahe and others) have quartz-carbonate sediment composition. It is interesting that in the case the maximum quartz content is noted in the coarse sand fractions (1-0.5 and 0.5-0.25 mm) while it is less in the finer fractions. This is apparently connected with the solution of quartz in the coastal zone and its "consumption" by several forms of diatoms.

Coral sands generally dominate, including a significant admixture of sponge spicules and foraminifera, and fragments of shells, bryozoans, and other marine organisms. Foraminifera sometimes emerge as the dominant component, comprising up to 80% of the sediment.

The sediments of the land reef-flat are close in composition to the beach deposits. They are somewhat thinner, and also contain a greater quantity of poorly rounded material, primarily coral fragments, which sometimes form extensive fields. In addition to the coralline component, there are numerous foraminifera, sponge spicules, and detritus of mollusk shells.

Island sands and sandstones are widely developed on low atolls, where they almost completely make up island land. On several atolls (Farquhar, Astov, Kosmoledo) they form an upper accumulative cover lying on the reef limestones. These are sediments of beach or storm ridges in origin, which are derived from the dynamic action of marine waves.

The deposits are represented by sands and sandstones. The latter are generally friable, rarely dense, medium and coarse grained, sometimes coarser, up to gravellites and conglomerates on the windward side of the islands. Their compositions are carbonate, coralline, seldom foraminiferal, including remnants of shells of mollusks, bryozoans, sponge spicules, fragments of chalcid algae, etc. On upland islands the deposits have a mixed quartz-carbonate composition. The sandstones formed at the level of the water table, where low magnesian calcite cement precipitates from fresh waters saturated by calcium carbonate.

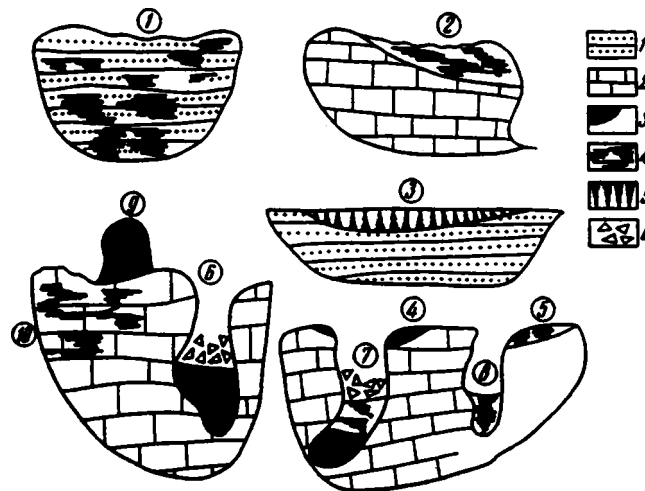


Fig. 2. Various types of phosphorite deposits from the Seychelles Islands: 1) island sandstones; 2) limestones of ancient reef; 3) concentrated phosphorites; 4) depleted phosphorites; 5) guano of various degrees of metamorphism; 6) varied detrital material. The circled numbers are the types of deposits: 1) aquatic in island sandstones; 2) subaquatic in relief depressions; 3) subaquatic accumulation of guano; 4) concentrated accumulation in relief depressions; 5) depleted deposit in relief depression; 6) concentrated and depleted deposits in karst cavity; 8) depleted deposit in karst cavity; 9) concentrated deposit in the form of a remnant relief mountain; 10) depleted deposit in reef limestone.

We also conditionally relate the sediments of the splash zone to the coastal marine deposits, although, strictly speaking, they have a more complex genesis. The wind also participates in their formation, which increases the power of fragment ejection by wave splashing. Deposits of this type are established along marine beaches of the islands of Saint Pierre, South Island (Aldabra), and Assumption, where they are concentrated in the form of individual hills ("pseudodunes") on deep cracks in the rear portion of abrasion terraces, or they form continuous narrow fields of "uplift" beach. The composition of this sand is grey, principally coarse and medium grained, sorted, with gravel, rarely with pebbles.

Shallow marine formations are one of the most widely distributed sediments of the coastal zone of the Seychelles Islands. Only mineral deposits of this type are developed on island land. They are represented by cemented rocks of the reef-flat developed on the floor surface of uplifted atolls. The conditions of sediment accumulation on the reef platforms, where reefogenic rocks are formed, are extremely varied. Close to shore, the outlying and partly dry portions of the reef-flat are occupied by fields of varied grained sands with fragments of corals and mollusk shells, which alternate with numerous remnants of sea week, partially cemented by products of the life action of blue-green algae. Seward, in the zone of greatest wave activity, accumulation of coarse coral fragments accumulating on the surface of the reef-flat is noted. This is the zone of maximal development of encrusting algae, which form algal mounds; maximal wave activity is observed here. On the reef's outer slope, where the majority of corals reside, not only their active growth occurs, but also their destruction. Detrital material is both supplied to the surface of the reef-flat and accumulated at the slope foot.

In lithological relations, the reefogenic rocks represent carbonate rocks of varied composition and degree of lithification with predominance of organogenic-detrital and algal limestones. Lithification is accomplished through processes of aquatic (chemogenic and biogenic) cementation. The first occurs in shallow water, well warmed portions, where thanks to photosynthesis, algae extract CO_2 from marine water. It converts to a supersaturated state and as a result carbonates precipitate first of all aragonite and high magnesian

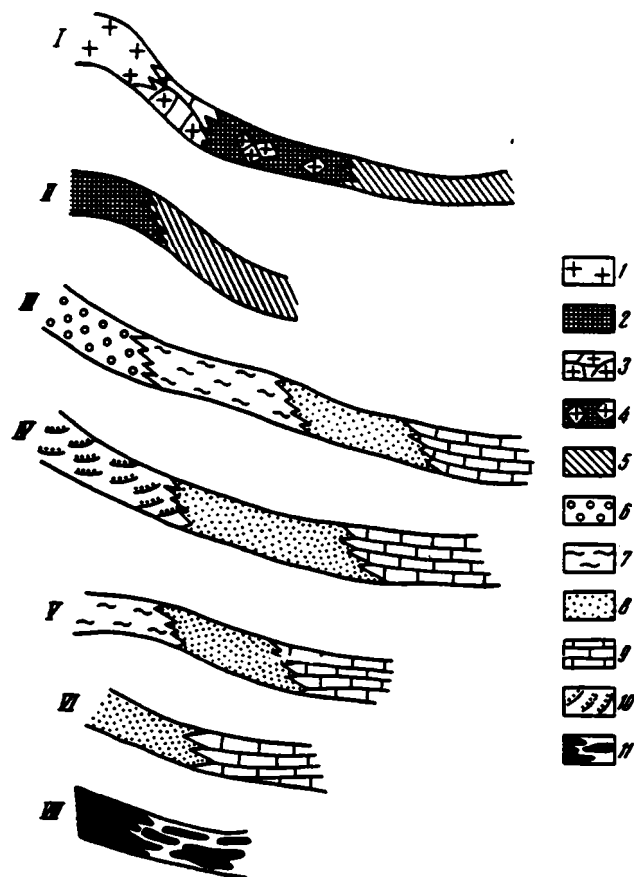


Fig. 3. Facies series of the most recent deposits of the Seychelles Islands. I-VII) facies series; deposit facies: 1) granites; 2) elluvial; 3) landslide (gravitational); 4) elluvial-gravitational; 5) talus; 6) alluvial; 7) lagoonal; 8) coastal marine (beach); 9) shallow marine (reef-flat); 10) eolian; 11) phosphorites.

calcite. These mineral phases form an isopachic bordering cement connecting the detrital material and filling spaces in the dead corals.

Biogenic cementation is basically due to the life activity of algae (blue-green and encrusting) surrounding and lithifying the products of destruction into dense carbonate rock. It is established that encrusting algae are most easily established in the zone of maximal hydrologic activity on marine parts of the reef, where the maximal degree of cementation is also noted.

As soon as reefogenic rocks emerge onto the surface and appear in the subaerial zone, their mineral composition is significantly altered. Recrystallization of aragonite and high magnesian calcite into low magnesian calcite with the formation of gravitational, meniscus, and drusy cements is accomplished under the actions of meteoric waters. In addition, active removal of Sr^{2+} ions carried out of the reefogenic rocks is noted, that is, the longer limestones undergo action of fresh water, the less strontium remains in them (see Table 3).

Biogenic island formations are interesting in their occurrence and practical significance. They are represented by guano and the products of its diagenesis: phosphorites. In various geomorphological positions (Fig. 2) they are noted on many low islands of the Seychelles bank, Amirante Islands, and islands of the Farquhar and Aldabra atolls. Phosphorites are the object of commercial development on several islands; it is true that the deposits are at the present time already exhausted to a significant degree. In lithological relations, these rocks represent phosphatic formations of various degree of concentration and consolidation, from friable brown to strong drainage rocks of dark-brown color. Thanks

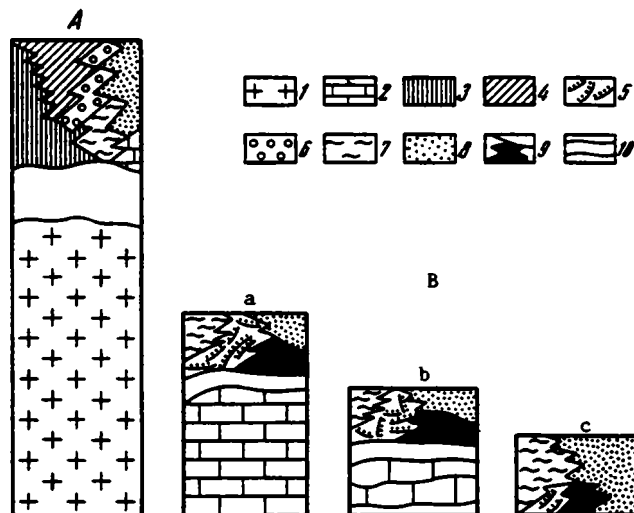


Fig. 4. Basic types of sections of the most recent deposits of the Seychelles Islands. Types: A) upland islands; B) atolls [a) uplifted; b) weakly uplifted; c) low]; 3-9) deposits of accumulative cover [3) weathering crust; 4) slope; 5) eolian; 6) alluvial; 7) lagoonal; 8) coastal-marine; 9) bioorganogenic-phosphorites]; 10) prolonged discontinuities.

to their resistance to destruction, dense phosphorites sometimes form residual mountain forms on beaches and land, in places of erosion and leaching of the rocks surrounding them.

The following phosphorites are distinguished in the classification of Yu. N. Zanin, allowing for type of texture: accretional, cavernous, pseudoolitic, homogeneous massive, and breccialike.

In the early stage of guano formation the most dissolvable components are withdrawn, leaving insoluble sediments of nonorganic calcium phosphates (brushite, monetite, and vitloquite). Further transformation of phosphates and their conversion to rock is connected with features of their dispersal mainly in a water medium (in both the vadose and phreatic zones) and conservation. On low islands in the process of interacting with meteoric waters phosphates migrating into island sands and sandstones form a cover crust of (atollic) phosphorites, sometimes covered by a layer of friable phosphorites which are the products of secondary weathering of dense phosphorite bearing rocks. Thicker sequences of phosphorites are noted on uplifted coral reefs. Here as a result of the substitution of carbonate rocks by phosphate, metasomatic rock occurrences are formed. Often the accumulation is accomplished by chemogenic means in karst cavities. Here phosphorites sometimes contain mineral remnants of crabs, tortoises, and skeletons of birds and mammals. It is interesting that during filling of karst cavities by bird droppings, ammonia is washed out of it, and the guano acquires an acid reaction, which in its turn promotes the solution of limestones and increase in the volume of the karst cavity.

Facies Series. The considered genetic varieties of the most recent deposits of the island land of the Seychelles Islands in their lateral extent comprise the determined facies series, which represent the natural paragenetic associations of the sediments (Fig. 3).

Series I is composed of various subaerial deposits: elluvial formations (weathering crusts) and the slope sediment series: landslide, elluvial-gravitational, and talus. The facies series is peculiar exclusively to the upland islands. It is expressed in overall form on Mahe Island. Series II is represented by weathering crusts, which in terms of facies transform into talus accumulation. It is characteristic of the outlying portions of the upland islands. Series III is the subaquatic-aquatic type, also developed on the upland islands, where an erosive network is available. It is composed of various facies of aquatic sediments: alluvial, lagoonal, coastal marine, and shallow marine. The first two facies comprise the subaerial branch of the series, and the latter the marine. Series IV

(subaerial-subaquatic) is principally represented by coastal marine deposits and the products of their wind redeposition (eolian). It is characteristic for parts of the Farquhar Islands and for all of the islands of the Aldabra atoll. Series V and VI are composed from a series of subaquatic-aquatic sediments: lagoon-coastal marine and shallow marine. The sediments of series V are developed on low islands of the Seychelles bank, the Amirante Islands, and islands of the Providence group Farquahar; the deposits of series VI are the most developed association of sediments on the Seychelles Islands, where they are almost universally recorded. On islands of the Aldabra group, and partially on Farquahar, it is distributed together with formations of series III. Last, series VII represents the short array of biological formations: the original product (guano) and the final product of its formation-phosphorites. The deposits have azonal distribution and are not noted on the upland islands, which have apparently been unfavorable for the recent existence of large bird colonies.

Series I and III paragenetic types of sediments comprise the so-called long series, which are composed of a greater number of facies and characteristic only for the large upland islands. The "short" facies series are typical for a majority of the islands. They are composed of two to three genetic varieties of sediments. Consequently, the varied facies composition of the most recent deposits is characteristic only for the island land of the large upland massifs of the Seychelles bank (the "microcontinent"), and on the whole for all other islands and atolls the genetic "set" of the sediments is scanty and composed principally of two to three facies of aquatic and subaquatic deposits.

On the whole the lithological features of the most recent deposits of the island land of the Seychelles Islands consist of the presence of three basic types of sections, united into two significantly different classes (Fig. 4). Type A is characteristic of the upland sediments, representing a "microcontinent" with a typical "set" of subaerial and surface water facies of sediments. Type B is developed on the low and uplifted reefs, and is composed principally of coastal marine and shallow marine facies.

The noted features are connected with the deciding influences of the following factors on the character of sediment accumulation: 1) type of structure; 2) signs and directions of neotectonic movement (this determines the class and section type of the deposits); the position in equatorial and subequatorial waters of the global oceans (reef, predominating organogenic-carbonate coastal marine and shallow marine sediments, the high degree of lithification of the rocks); the small area of island land (constricted facies series, relatively poor sorting of surface water deposits); the position of a portion of the islands in the zone of southeast trade winds (the development of eolian processes).

The distribution of Co in crusts and nodules on submarine seamounts and deep basins of the Pacific Ocean, and its relationship to the principle ore components and to several other metals, are examined.

Of the four main ore components in oceanic ferromanganese crusts and concretions (Mn, Cu, Ni, Co), the latter, because of its low content and relatively high value, will probably be of most economic interest in the future. The behavior of Co in oceanic sedimentary ore processes is still open for discussion.

It has long been known that, unlike nickel and especially copper, cobalt has a clear tendency to concentrate in ore crusts and nodules on submarine seamounts [4, 5, 9, 22, 24, etc.] and has an inverse association with depth. The chemical composition of Co-enriched ore crusts on seamounts in the central Pacific has been the subject of a number of papers [3, 12, 19, 20, 23, 28, etc.].

There are several patterns of distribution of Co in Pacific crusts and nodules [8, 21, 38]. Taking into account the relationship of Co content to depth, as well as the increase in content with decrease in the depth of submarine rises (seamounts and ridges), we have constructed a map in an attempt to show both the background values of Co in crusts and nodules on the floor of deep basins, but also its content on seamounts (Fig. 1). An analysis of the distribution of Co with depth, discussed below, show that at depths of more than 3000 m the content is usually close to background for nodules and crusts on the ocean floor. Therefore, the scale symbols on the map indicate rises with depths of less than 3000 m. Values greater than background (0.5-0.75%) are found relatively rarely below 3000 m; these localities, also generally associated with rises, are given special symbols (see Fig. 1).

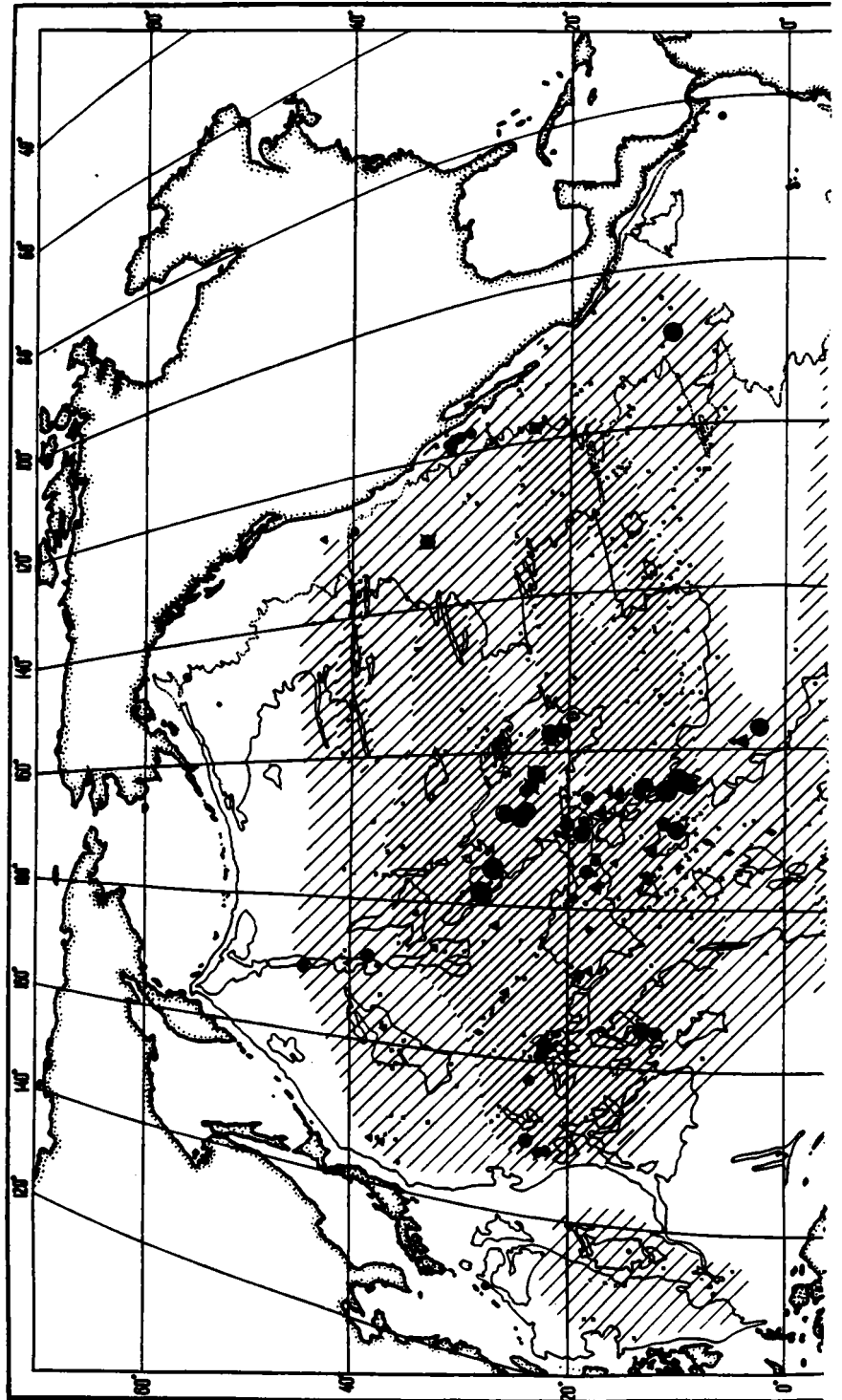
The similarity in chemical composition between mineralized crusts and sedimentary concretions found with them on both seamounts and the ocean floor [3, 5, 8, 19, 28, 38] justifies their being considered together. The background content of Co in concretions in deep basins and rises at depths of more than 3000 m is usually no more than 0.5%. Relatively high (0.25-0.5%) values of Co are found in concretions in pelagic clays in the southern part of the Penrin basin, the South basin, and the northern part of the Central basin. Moreover, in the South basin values of 0.4 to 0.5% are found quite frequently. Lower values of Co, <0.25%, were found in diagenetic concretions of the equatorial belt of radiolarian ooze in the southeastern part of the ocean [39] and on the margins of the pelagic zone.

Against this background there is a clearly expressed increase in Co in nodules and crusts on local rises in all regions (both in the pelagic zone and in near-continent areas). The tendency for an inverse relationship of Co concentration with depth has been observed at hypsometric levels of basin floors, where sedimentary concretions on hills are somewhat enriched in Co [5, 6, 27]. This is particularly true in the radiolarian belt, where in diagenetic nodules on gently rolling plains and in sedimentary nodules on abyssal hills 200-600 m high the Co content increases by 1.5-2.0 times [5, 7]. But this trend is especially clear-cut on submarine seamounts and ridges, whose peaks and crests are less than 2 km deep.

The map shows maximum values for Co at minimum depths for each seamount. The scale of the map does not permit an analysis of variations in Co content for each individual seamount, but it demonstrates the general trend of variation with depth of rise.

Halbach and Puteanus [12] have noted the presence of two generations of crusts, which differ in composition. According to their data, the older crusts are impoverished in Fe and Co. Both younger and older generations of mineralized crusts on seamounts contain inter-

Institute of Oceanology, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 106-121, March-April, 1989. Original article submitted April 25, 1988.



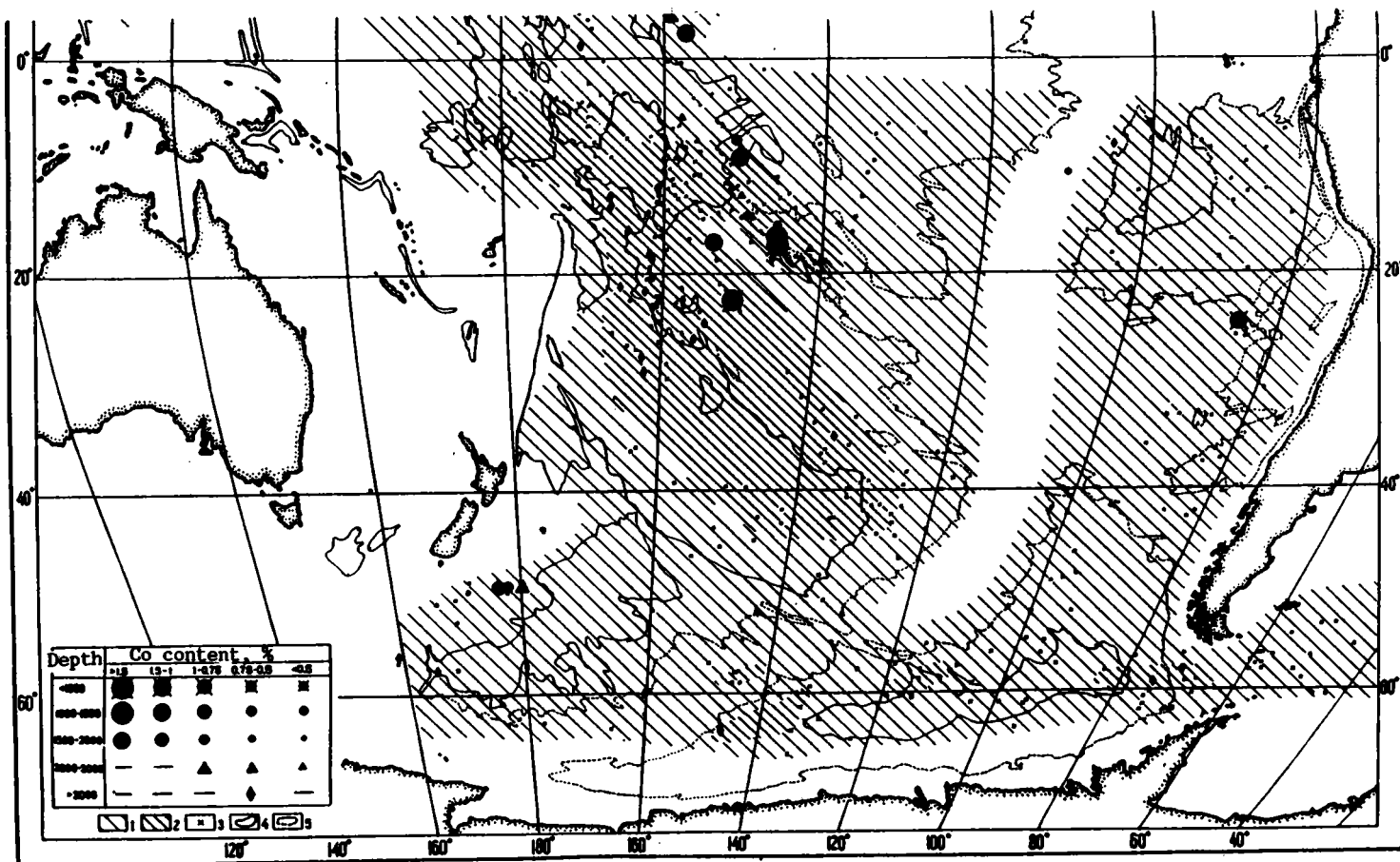


Fig. 1. Map of Co distribution, in %, in Pacific nodules and crusts (scale symbols give Co content for submarine rises by depth, diagonal lines give background content of Co in deep basins). 1) Less than 0.25%; 2) 0.25-0.5%; 3) location of analyzed samples; 4-5) isobaths [4) 500 m; 5) 4000 m].

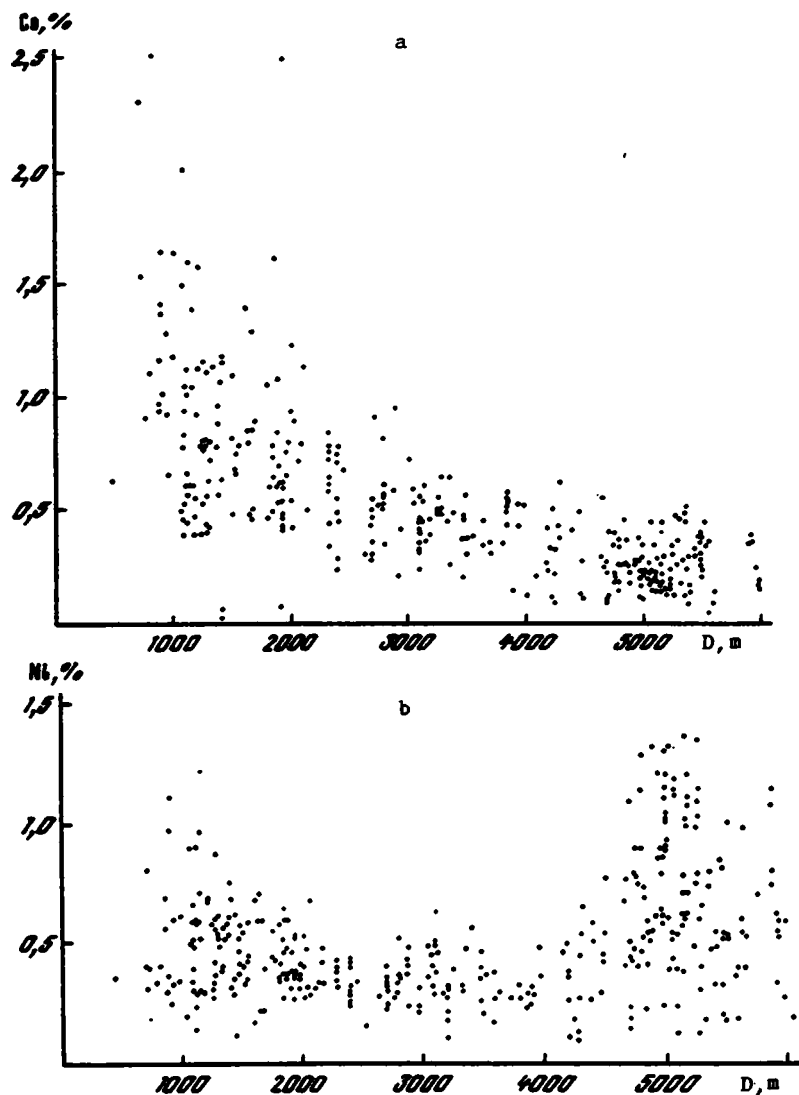


Fig. 2 (a, b)

beds of phosphatized limestone. Similar variations in composition and the occurrence of phosphate have been noted in thick ore crusts on the guyots IOAN and Ita Maitai [3] and on the Mid-Pacific ridge, according to information obtained by the research vessel "Vityaz'" [2, 4]. Construction of the map and statistical analyses presented in this article were based on data on nodules and younger mineralized crusts up to 3-5 cm thick [4, 12, 20, 23, 30-36].

Higher levels of Co ($>1.0\%$) are generally restricted to submarine rises with depths of less than 1500 m, and the highest levels (up to 2.5%) are at depths of less than 1000 m. At greater depths the Co content falls off steadily, and at depths of more than 2000 m it usually does not exceed 1.0% , while at more than 2.5 km it is less than 0.6% (Fig. 2a).

The relationship between Co content and depth (see Fig. 2), considered for the pelagic regions of the ocean, also show a major variation in its concentration at these depths. Thus, at depths of less than 1000 m the Co content ranges from 0.6 to 2.5% , at 1000-1500 m from 0.2 to 2.0% , at 1500-2000 m from 0.6 to 1.6% , and at 2000-3000 m from 0.17 to 1.23% (Table 1).

The map (see Fig. 1) also shows the restriction of high values of Co ($>1\%$) to crusts and nodules of seamounts (at depths of less than 2000 m) in the central part of the ocean: the eastern Mid-Pacific ridge, Hawaiian rise (south of 28° N. lat.), Line Islands, and The Tubuai-Tomaotu region. At the same depths in areas peripheral to the pelagic zone the Co content is lower, and does not exceed 0.75% (see Fig. 1). In shallow-water crusts and nodules on the continental rise, it is generally less than 0.5% (according to [21], it averages 0.419%).

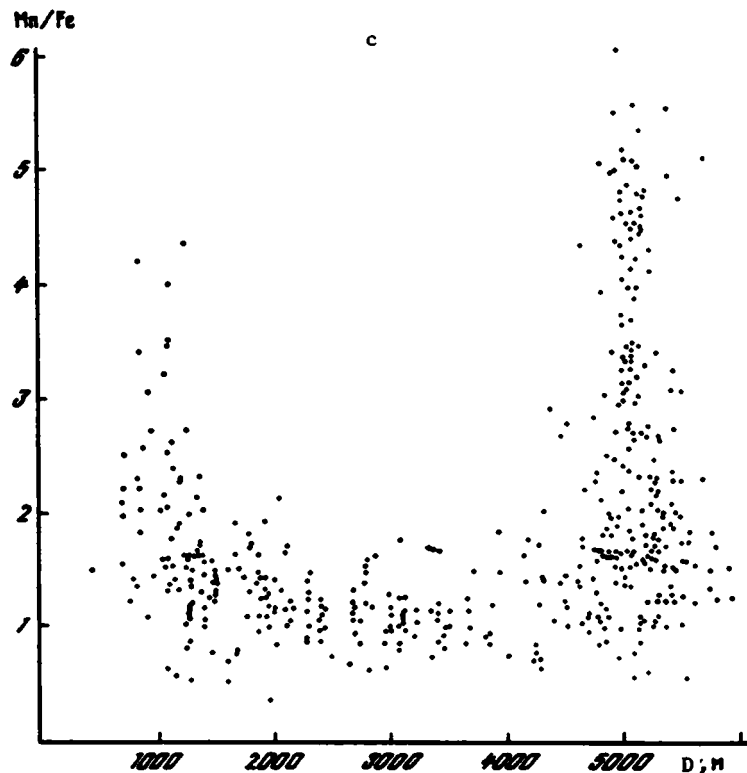


Fig. 2. Variation in content of Co (a) and Ni (b) and the ratio Mn/Fe (c) with depth D.

The distribution pattern of Co appears clearly on graphs of the frequency distribution of its content with depth (Fig. 3, Table 2). The graphs were compiled using samples of crusts and nodules on seamounts in the pelagic zone at depths of less than 1000 m, 1000-1500 m, 1500-2000 m, 2000-3000 m, 3000-4000 m, and adjacent regions of deep basin sea floor (central, northwestern, eastern, Penrin, southern) at depths of 4000-5000 m and greater than 5000 m.

The frequency curves of Co with depth are similar, with sharply expressed maxima for high Co content (less than 1% in 63% of the samples) at depths of less than 1000 m and minima at depths of more than 5000 m (in 59% of the samples). But at depths of 1000-1500 m the maximum values are already found in just 24% of the samples, and at 1500-2000 m, in only 10%. The maximum frequency (28-44%) encountered at 2000-3000 m corresponds to a Co content of 0.5-0.75%. With an increase in depth the frequency falls to less than 0.5%. At depths of 3000-4000 m a sharp decrease in Co takes place with a maximum frequency (76% of the time) in the range of 0.25-0.5%.

The typical composition of ferromanganese deposits on seamounts is presented in Table 1, and Fig. 3 gives the frequency distribution of the Mn, Fe, Cu, Ni, Pb, and Ti content with depth. As these data show, nodules and crusts on seamounts are characterized by high Mn and Pb content, and relatively high Ni (see Table 2) and Mo [7]. Comparison of the frequency distribution data (see Fig. 3) shows a distinct connection between the Co and Mn contents. The diagram for Mn essentially repeats the curves for Co, with a maximum frequency at high (>25%) values for Mn at depths of less than 1000 m and subsequent shifts to lower levels of the element. At depths of 3000-4000 m, just as in the case of Co, a sharp maximum (66% of the samples) is noted in the area of relatively low content (15-20%), which is more typical of oceanic values of Mn, close to its content in sedimentary concretions on the floor of deep basins. A secondary maximum for high Mn content at depths of more than 5000 m is restricted to diagenetic nodules of the radiolarian zone.

A direct connection between Co and Mn in crusts and nodules on seamounts is supported by a diagram of their relationship (Fig. 4a) and by correlation coefficients (Table 3, 4).

The decrease in Co content in nodules from deep basins is associated with changes in the correlations, with high positive values of the coefficients for Co and Fe in diagenetic concretions [7].

TABLE 1. Variation in Composition of Pacific Crusts and Nodules with Depth

Parameter	Mn	Fe	Co	Ni	Cu	Pb	Ti	Mn/Fe
Less than 1000 m ($n^* = 17$, $n^\dagger = 8$)								
$\bar{x}$	24.84	13.1	1.28	0.51	0.05	-	1.01	2.1
S	4.48	4.44	0.55	0.23	0.02	-	0.22	1.08
V	18.0	33.9	4.29	46.0	49.9	-	22.3	40.3
$X_{\min}$	16.07	6.2	0.62	0.26	0.015	-	0.67	1.08
$X_{\max}$	33.0	22.4	2.57	1.1	0.12	-	1.28	4.2
1000-1500 m ($n^* = 67$, $n^\dagger = 25$, $n^\ddagger = 44$)								
$\bar{x}$	21.5	13.92	0.75	0.50	0.08	0.168	1.0	1.64
S	5.75	3.72	0.36	0.18	0.05	0.048	0.29	0.81
V	26.7	26.7	47.8	38.7	71.7	28.7	29.4	49.1
$X_{\min}$	8.0	6.02	0.20	0.03	0.011	0.07	0.59	0.50
$X_{\max}$	33.92	21.0	2.00	0.97	0.26	0.50	1.64	4.37
1500-2000 m ($n^* = 42$, $n^\dagger = 11$, $n^\ddagger = 25$)								
$\bar{x}$	18.95	15.52	0.68	0.43	0.086	0.176	1.06	1.25
S	4.79	2.83	0.29	0.13	0.05	0.057	0.22	0.39
V	25.3	18.2	43.3	29.7	59.5	32.4	21.1	31.6
$X_{\min}$	6.0	9.8	0.06	0.17	0.015	0.092	0.73	0.33
$X_{\max}$	27.2	22.6	1.60	0.71	0.24	0.26	1.83	2.74
2000-3000 m ($n^* = 54$, $n^\dagger = 42$, $n^\ddagger = 47$)								
$\bar{x}$	19.3	17.55	0.54	0.35	0.14	0.118	1.23	1.15
S	4.39	2.57	0.21	0.086	0.084	0.043	0.26	0.30
V	22.8	14.6	39.5	24.2	60.2	36.6	21.5	26.6
$X_{\min}$	10.19	9.6	0.17	0.16	0.036	0.031	0.51	0.59
$X_{\max}$	27.2	22.7	1.23	0.68	0.36	0.23	1.74	2.09
3000-4000 m ($n^* = 51$, $n^\dagger = 23$, $n^\ddagger = 44$)								
$\bar{x}$	17.9	17.06	0.40	0.37	0.16	0.117	0.98	1.08
S	2.88	2.38	0.105	0.10	0.071	0.062	0.24	0.26
V	16.1	13.97	25.9	27.18	44.7	52.8	25.3	24.13
$X_{\min}$	11.09	12.58	0.13	0.19	0.058	0.045	0.40	0.68
$X_{\max}$	24.1	22.8	0.63	0.65	0.40	0.27	1.48	1.80
4000-5000 m ($n^* = 73$, $n^\dagger = 33$, $n^\ddagger = 49$)								
$\bar{x}$	17.72	13.0	0.30	0.59	0.40	0.076	0.87	1.35
S	3.64	3.27	0.137	0.26	0.23	0.039	0.39	0.67
V	20.5	25.2	44.7	43.2	57.6	51.3	44.85	44.6
$X_{\min}$	7.8	5.58	0.063	0.12	0.04	0.02	0.21	0.60
$X_{\max}$	29.6	20.21	0.88	1.33	1.11	0.15	2.15	4.55
More than 5000 m ($n^* = 210$, $n^\dagger = 122$, $n^\ddagger = 104$)								
$\bar{x}$	20.95	9.68	0.24	0.81	0.67	0.066	0.62	2.6
S	4.93	3.69	0.09	0.33	0.38	0.038	0.29	1.50
V	23.5	38.1	40.1	41.02	56.7	57.6	47.03	57.6
$X_{\min}$	5.0	3.3	0.02	0.07	0.05	0.09	0.14	0.50
$X_{\max}$	33.7	27.8	0.51	1.72	1.85	0.22	1.8	9.4

Note. * Number of analyses for Mn, Fe, Co, Ni, and Cu; † for Pb; ‡ for Ti.

Craig et al. [20] have found a connection between Co content and the Mn/Fe ratio in ore crusts on the Hawaiian chain. According to Halbach and Puteanus [12], the Mn/Fe ratio in crusts in the central Pacific ranges from 1 to 3.4. Our data on crusts and nodules on seamounts in the pelagic zone (Fig. 2b) show a range in the Mn/Fe ratio of 0.5-4.3, with a maximum frequency for the higher values (47% of the samples) at depths of less than 1000 m (see Fig. 3) and a progressive decrease with an increase in depth. The most typical Mn/Fe ratio at depths of 1500-4000 m are less than 1.5 (see Fig. 3), with a frequency of more than 80%; a secondary maximum (>2) applies to concretions on the floor of deep basins, at depths of more than 4800 m (see Fig. 2c).

The data presented in Fig. 4b and Tables 3 and 4 clearly show a relationship between Co in nodules on seamounts and the Mn/Fe ratio. The Co content generally increases with an increase in the Mn/Fe ratio. This relationship is not found everywhere, however, as shown by

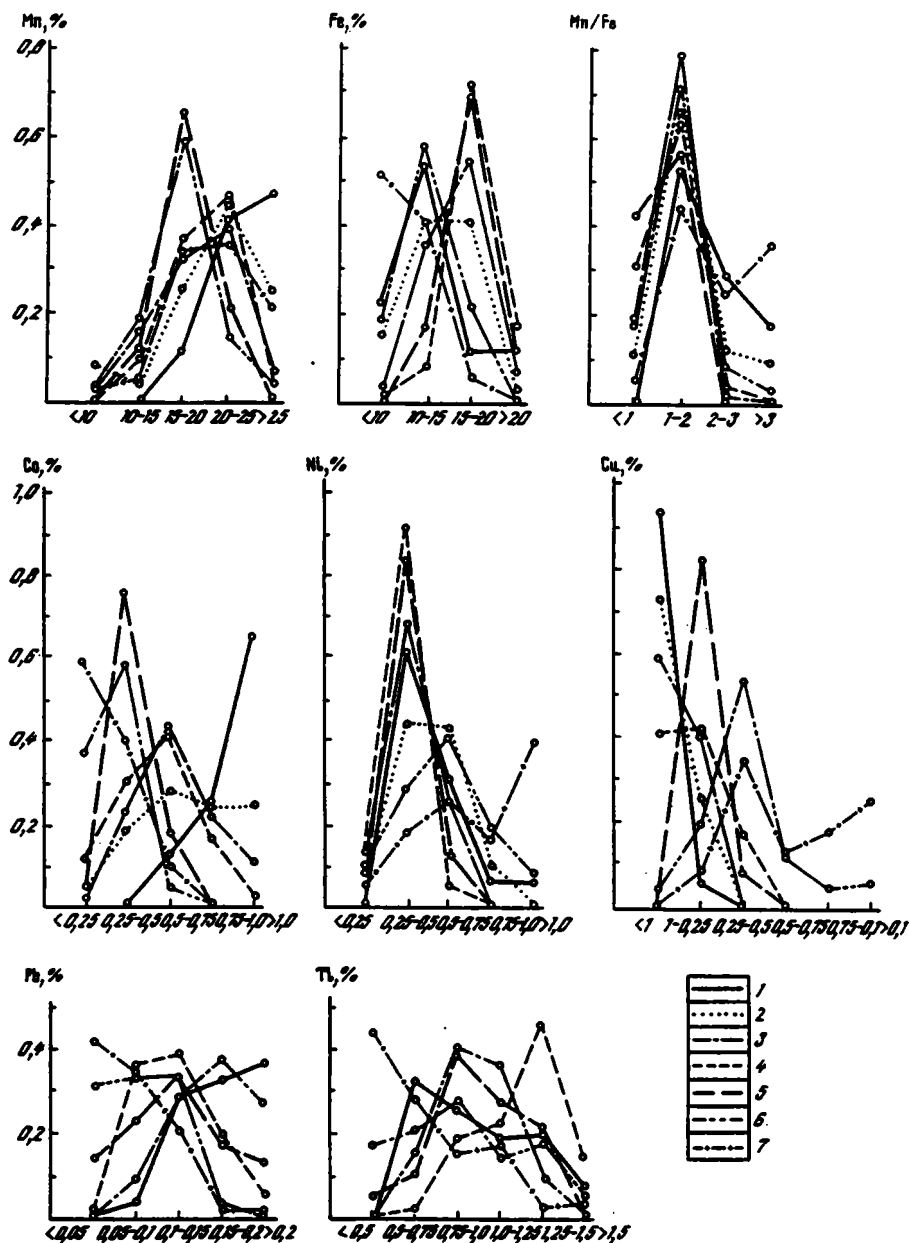


Fig. 3. Frequency distribution of Mn, Fe, Mn/Fe ratio, Co, Ni, Cu, Pb, and Ti with depth. 1) Less than 1000; 2) 1000-1500; 3) 1500-2000; 4) 2000-3000; 5) 3000-4000; 6) 4000-5000; 7) more than 5000 m. For Pb and Ti, symbol No. 1 is 1500 m.

a decrease in the correlation coefficient of Co-Mn/Fe relative to Co-Mn. A relatively low (0.45-0.65) Co content is found in shallow-water nodules and crusts in the region peripheral to the pelagic zone, with Mn/Fe values of 2-4 (see Figs. 1 and 4b).

Seamount nodules and crusts that are enriched in Pb have frequency distributions similar to that of Co (see Fig. 3), and are sharply impoverished in Cu. The most common minimum values (<0.1%) of Cu are found at depths of less than 2000 m; they are found in 94% and 74% of the samples at depths of less than 1000 m and 1000-1500 m (see Fig. 3). With an increase in depth the Cu content gradually increases, and at depths of 2000-3000 m and 3000-4000 m magnitudes of 0.1-0.25% are found in 42 and 82% of the samples, respectively (see Fig. 3, Table 1). In nodules in deep basins, at depths of more than 5000 m, the Cu content generally exceeds 0.5% and reaches maximum values (>1%) in diagenetic concretions in the radiolarian belt at depths of more than 4800 m. Variations in Cu content in nodules on seamounts are independent of the Mn content or the Mn/Fe ratio (see Tables 3, 4).

TABLE 2. Number of Analyses Used in Construction of Frequency Distributions of Metals in the Pelagic Zone

Depth, m	Number of analyses		
	crusts	nodules	total
Submarine seamounts			
<1000	17	-	17*(2)† 8‡
1000-1500	49	18	67(23) 44
1500-2000	33	9	42(11) 25
2000-3000	41	13	54(42) 47
3000-4000	27	24	51(23) 44
Deep basins			
4000-5000	10	63	72(33) 49
5000	-	210	210(122) 104

*Number of analyses for Mn, Fe, Ni, Cu, Co; †for Pb; ‡for Ti.

With respect to depth, Ni differs from Co and Cu, and is similar to Mn and with the Mn/Fe ratio (see Fig. 2b). Two maxima are recognized, one of which is restricted to ferromanganese deposits on seamounts at depths of less than 2000 m, and the other to the floor of deep basins. On seamounts, the distribution of Ni is similar to that of Co and Mn, with some displacement of its maximum concentration toward greater depths than in the case of Co (see Fig. 3). The Ni content in nodules and crusts on seamounts ranges from 0.15 to 1.1%, with maximum frequency found in the higher values (>0.5% in 51% of the samples) at depths of 1000-1500 m and a gradual decrease with increasing depth. At depths of 2000-4000 m, the Ni content is 0.25-0.5% in 90-82% of the samples. Such low Ni values (<0.5%) are also common in shallow-water concretions with maximum values of Co (>1%), except for crusts of the northern part of the Hawaiian rise which are enriched in Co and Ni (0.5-1.1%) [20].

With a decrease in Co content in shallow-water concretions (at depths of <2000 m) the amount of Ni increases and commonly is as much as the Co or even more. For example, along the western margin of the Mid-Pacific ridge, at depths of 1000-1100 m, the Ni content is 1.5-2 times greater than Co (0.38-0.61% Co and 0.52-0.90% Ni).

Thus, in nodules and crusts on seamounts, Co, Ni, and Pb have an inverse correlation with depth: their content decreases as depth increases. A sharp decrease in Co takes place at 2000-2400 m and it reaches a minimum in deep-water crusts and concretions (see Fig. 2). At these same depths (>2000 m) a decrease in Ni occurs, although more gradually, and then (at 4000 m) it increases again (see Fig. 2b).

The Co and Ni content in ferromanganese deposits on seamounts is affected by both Mn and the Mn/Fe ratio, but the size of the correlation coefficient for Co and Mn/Fe is lower.

As shown by analysis of numerous samples of ore crusts and nodules on seamounts, their composition is not related to that of the underlying rocks or to the nuclei of the nodules. As noted above, the data used in this study are from relatively young ore crusts (2-3 cm thick, rarely as much as 5 cm), so compositional variations should not be age-related. This can be reliably confirmed for crusts from the Line Islands, Hawaiian rise, and Mid-Pacific ridge, from which the bulk of the analyses used were obtained [4, 12, 19, 20].

Variations in the chemical composition of ore deposits on seamounts with depth are not related to their mineralogical composition, since apart from their relationship to depth the ores are composed mainly of poorly crystallized hydroxides of Mn and Fe. The basic Mn mineral on seamounts is vernadite, which occasionally reveals a 10 Å phase [19, 20]. X-ray diffractometer and electron microscope studies conducted by T. Yu. Uspenskaya on ore crusts and nodules from a central Pacific guyot showed an increase in vernadite crystallinity (pure Mn phase and vernadite closely intergrown with Fe hydroxides) with an increase in the Mn/Fe ratio and the presence of a small amount of asbolite-buzerite. Fe-phase crusts and nodules on seamounts are fine-grained unordered oxyhydrates ($\text{FeOOH} \cdot n\text{H}_2\text{O}$) [16], occasionally with goethite [6, 20, etc.].

The statistical results presented herein, together with data provided by other authors [22, 24, 30, etc.], suggest three main patterns of behavior of cobalt in ferromanganese ore processes on seamounts.

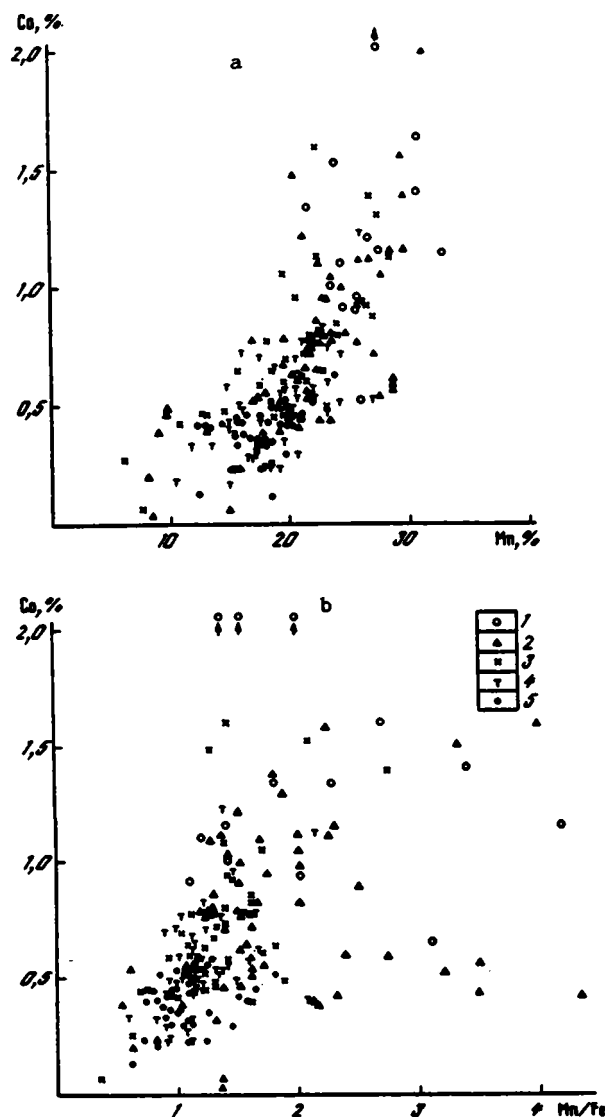


Fig. 4. Relationship between Co and Mn (a), and between Co and Mn/Fe ratio (b), in crusts and nodules on seamounts at various depths. 1) Less than 1000; 2) 1000-1500; 3) 1500-2000; 4) 2000-3000; 5) 3000-4000 m.

1. Concentration of Co in ore minerals of ferromanganese crusts and nodules increases with a decrease in absolute depth, with maximum concentration ($>1\%$) almost always at the mountain crest. The tendency for an increase in Co concentration with a decrease in relative depth (from the foot to the crest) is observed at various absolute depths including abyssal hills on the floor of deep basins at depths of more than 4000 m, although its concentration at great depths does not exceed background values.

2. Cobalt in ferromanganese crusts on seamounts has a positive correlation with the Mn content and the Mn/Fe ratio, i.e., with the proportion of manganese hydroxide phases, occurring predominantly as vernadite. An increase in the iron phase (with a corresponding decrease in the Mn/Fe ratio) is accompanied by a decrease in the Co concentration in both the ore and with respect to the manganese phase. Increase in the concentration of Co, as in Pb and Ni (with some shift in the maximum concentration with respect to Co), is accompanied on seamounts by a sharp decrease in the Cu content.

3. High Co concentrations are typical of seamount ore crusts in the pelagic zone of the Pacific, with its maximum in the central areas. The ore crusts of the ocean margins, as well as hydrothermal crusts of the rift zones at comparable depths, are cobalt-poor.

TABLE 3. Correlation Coefficients for Metals in Ferromanganese Nodules and Crusts at Various Depths in the Pacific Ocean

Element pairs	Depth, m					
	1500 n = 83	1500-2000 n = 39	2000-3000 n = 54	3000-4000 n = 50	4000-5000 n = 73	5000 n = 210
Mn-Fe	-0,028	0,047	0,013	0,008	-0,371**	-0,556*
Mn-Co	0,593**	0,47**	0,426**	0,583**	-0,033	-0,189
Mn-Ni	0,530**	0,59**	0,565**	0,411**	0,695**	0,794*
Mn-Cu	-0,137	-0,11	0,016	-0,068	0,601**	0,768*
Mn-Ti	-0,547**	-0,046	0,428**	0,147	0,045	-0,368**
Mn-Pb	0,273*	0,154	-0,367**	-0,432**	-0,078	-0,249*
Fe-Ca	0,041	-0,261	-0,121	0,123	0,249*	0,673**
Fe-Ni	-0,407**	-0,364	-0,409**	-0,372**	-0,614**	-0,781**
Fe-Cu	-0,132	-0,391*	-0,018	-0,350*	-0,635**	-0,807**
Fe-Ti	0,147	0,349	0,349*	0,427**	0,593**	0,831**
Fe-Pb	0,196	-0,147	0,157	-0,025	0,281*	0,706*
Co-Ni	0,207	0,349	0,287*	0,065	-0,139	-0,454*
Co-Cu	-0,242*	-0,277	-0,489**	-0,284*	-0,250*	-0,570**
Co-Ti	-0,187	-0,187	0,048	0,597**	0,617**	0,619*
Co-Pb	0,089	0,705**	0,181	0,390**	0,126	0,572**
Ni-Cu	0,280*	0,312	0,059	0,346*	0,850**	0,925**
Ni-Ti	-0,497**	-0,079	0,104	-0,324*	-0,201	-0,627**
Ni-Pb	-0,043	0,274	-0,472**	-0,088	-0,277*	-0,503**
Cu-Ti	-0,0353	-0,269	0,241	-0,409**	-0,437**	-0,632**
Cu-Pb	0,089	0,023	-0,315*	-0,333*	-0,324**	-0,567**
Ti-Pb	-0,629**	0,459**	-0,191	0,349*	0,221	0,544**
Mn/Fe-Co	0,295**	0,545**	0,395**	0,380**	-0,285*	-0,491**
Mn/Fe-Ni	0,608**	0,739**	0,691**	0,567**	0,772**	0,824**
Mn/Fe-Cu	0,054	0,108	-0,077	0,209	0,827**	0,853**
Mn/Fe-Ti	-0,481**	-0,213	0,110	-0,109	-0,448**	-0,616**
Mn/Fe-Pb	-0,071	0,261	-0,342*	-0,323*	-0,335**	-0,530**

Note. n is number of analyses at all depths for Mn, Fe, Ni, Co, Cu; also for Pb and Ti (see Table 2).

*Correlation value for $p = 0.05$; **Same for $p = 0.01$.

Various authors have attempted to explain these patterns. The close correlation (and evident genetic association) between Co and manganese phases require first of all an explanation of the cause of enrichment of seamount ore crusts (at depths of 1500-2000 m) in manganese; that is, the inverse relationship between Mn (and Mn/Fe) and depth.

Piper and Williamson [38] were the first to point out the vertical zonation of ore formation, especially the increase in the Mn/Fe ratio, at depths of 500-1500 m and more than 3000 m. The increase in Mn/Fe in shallow-water ferromanganese deposits was ascribed by these authors to the breakdown and release of metals from the soft parts of organisms, an increase in Mn/Fe and the Ni and Cu content, and changes in the distribution of rare earths at depths of more than 3000 m, with the supply of these metals by way of fecal pellets and a sharp increase in the rate of solution of carbonate shells at the lysocline.

Halbach and Puteanus [12] ascribed high levels of Mn and Mn/Fe in seamount nodules at 1500-2000 m or less to an increase in soluble Mn^{2+} in the minimum oxygen zone followed by its catalytic oxidation.

The increase in Mn content in the minimum oxygen layer (with a decrease in O_2 to below 100 mmole/kg the content of Mn(II) is 1-2 mmole/kg as opposed to 0.4-0.6 mmole/kg in higher layers of water) as a result of the breakdown of organic matter and the reduction of MnO_2 has been noted in a number of papers [26, 31, 33, etc.].

While not rejecting the role of the oxygen minimum in the formation of manganese-rich shallow-water crusts on seamounts, Alpin and Cronan [19] proposed the horizontal transfer of Mn by advection-diffusion from reduced near-continent sediments at depths of 500-2000 m [34]. With an increase in O_2 content below the oxygen minimum zone, catalytic oxidation on Mn(II) to oxyhydrate of Mn(IV) takes place.

As a result, on the crests of mountains that rise to the lower boundary of the oxygen minimum layer, favorable conditions should exist for relatively high concentrations of Mn

TABLE 4. Average of Correlation Coefficients for Metals in Ferromanganese Nodules and Crusts on Seamounts (at depths of 600-4000 m)

	Mn	Fe	Co	Ni	Cu	Ti	Pb	Mn/Fe	Depth
Mn	-								
Fe	0,138	-							
Co	0,589**	-0,269**	-						
Ni	0,580**	-0,503**	0,363**	-					
Cu	-0,210*	0,072	-0,445**	-0,002	-				
Ti	-0,138	0,319**	-0,025	-0,334**	0,049	-			
Pb	0,043	-0,212*	0,408**	0,227*	-0,379**	-0,217*	-		
Mn/Fe	0,670**	-0,718**	0,465**	0,683**	-0,151	-0,291**	0,162	-	
Depth	-0,346**	0,412**	-0,528**	-0,388**	0,494**	0,046	-0,391**	-0,438**	-

Note. For Mn, Fe, Co, Ni, Cu, n = 230; for Ti, n = 167; for Pb, n = 99.

*p = 0.05, r = 0.195; **p = 0.01; r = 0.254.

in ore crusts formed there. With an increase in depth, this effect gradually subsides and the Mn/Fe ratio decreases, at depths of 2000-4000 m (and for ore crusts on the ocean floor, 6000 m) becoming essentially constant, close to unity. From this it can be assumed that the relationship between Mn and Fe in ore crusts on seamounts is related to their relationship in the seawater. However, considering the overall very low Mn(II) concentrations, even those in the minimum oxygen layer, the formation of high-manganese ore crusts may be associated not so much with variations in the manganese concentration in the water as with variations in physicochemical environment (pH and Eh) determining its solubility.

The vertical variation in content of minor elements in crusts and nodules on seamounts is related to the content of the principal ore elements (Mn and Fe). As newly formed colloidal manganese and iron oxides are deposited, the minor elements are absorbed and deposited with them. Experimental work has established a high absorption capacity of nodules for cations of light metals. The similar nature of the exchange of light metals in nodules and synthetic manganese dioxides suggests that the absorption capacity of nodules is determined by the manganese state [13]. This hypothesis is also supported by the correlation coefficient of the metals and Mn (see Tables 3 and 4). A significant positive correlation of Co and Ni with Mn suggests that with an increase in the content of vernadite, the main manganese mineral in seamount ore deposits, there will be an increase in Cu and Ni. There is evidence that Co and Ni are extracted from seawater at higher valences [15, 25]. Other data show that Co and Ni are absorbed from seawater as the hydrated ions Co^{2+} and Ni^{2+} . Because of the high chemical potential of MnO_2 , the cobalt is oxidized by surface colloidal chemistry processes to Co^{3+} and enters the vernadite structure [16, 37]. This may be one of the main causes of the predominance of Co over Ni [12]. The decisive factor that determines the Co concentration in seamount crusts, according to Halbach and his coauthors [12, 29], is their rate of growth. The Co concentration increases as the rate of growth of the ore crusts decreases. The rate of growth, in turn, decreases with a decrease in depth, mainly as a result of the curtailment of the Fe supply in biogenic carbonate, the rate of solution of which increases with depth. These authors have suggested that the amount of absorption flow of Co to Mn(IV) hydroxide is independent of depth. At first glance, their hypothesis explains the general trend of vertical zonation (a decrease with depth) and circumcontinental zonation (restriction of high concentration of Co to the pelagic zone) of the Co content in ferromanganese deposits of seamounts. However, the proposal of an inverse relationship of cobalt concentration to the rate of growth (with constant deposition) is contradicted by data on thickness of ore crusts.

The thickest ore crusts are generally found on the crests of the seamounts, at depths of less than 1000-2000 m, where they are enriched in Mn and Co. Farther down the slopes (but sometimes on the crests) of seamounts at depths of ~2000-4000 m where ferriferous (Mn/Fe = 1-1.5) low-cobalt crusts are formed, their thickness is substantially reduced, apparently because of slow growth. These variations in thickness and composition of the crusts may be more readily explained by a somewhat increased deposition of Mn at lesser depths (because of the oxygen minimum layer), than by variations in the rate of supply of Fe from solution of biogenic carbonate. Variations in intensity of solution of CaCO_3 at depths above the foraminifera lysocline due to this effect have little influence.

In our view, the Co content of ore crusts on seamounts is determined by its absorption nature relative to Mn and to its distribution in the seawater column. This is supported by the similarity in the solution profiles of Mn and Co in seawater, with their sharp decrease in content below the oxygen minimum zone [19, 31, 32]. The proportion of the principal ore elements is also an important factor. As the iron content in ore crusts increases and ferriferous vernadite is formed [11], or with epitaxial growth of Mn and Fe oxyhydrates [17], there is apparently a decrease in the absorption capacity of Mn relative to the minor elements.

As regards the vertical zonation of the minor element content, and especially the shift in maximum concentration of Co and Ni, it can perhaps be explained by both the properties of the sorbent itself and the physicochemical conditions of ore mineral deposition, and the different biophilia of the minor elements (with an increase in the series Co-Ni-Cu) and the time of their regeneration [18, 19].

Laboratory experiments [1] have shown that the rate of absorption of Cu, Ni, and Co by synthetic Mn oxide increases with an increase in its oxidation. When oxidation approaches levels typical for oceanic oxyhydrates, the absorption rate of Co increases sharply, passing

that of the other two metals. When data on the increased degree of oxidation (oxygen content) of Mn oxyhydrates in ore crusts from the base to the crest of seamounts is considered for one of the Pacific guyots [10], it is verified that the preferential absorption of Co by the highly oxidized oxyhydrates on the crest may be one of the factors controlling the vertical variation in the composition of the ore encrustations.

On the basis of the data presented, together with information provided by other workers, it is concluded that regional patterns of distribution of Co in ore crusts on seamounts is determined by the position of the oxygen minimum and by the related manganese content in the seawater column, or (considering the negligible Mn concentration even at the oxygen minimum layer) by variations in the physicochemical parameters determining deposition rates.

Local variations in composition of ore crusts (Mn, Mn/Fe, Co) at these depths around individual rises are determined by fluctuations in bottom conditions of ore crust growth: variations in velocity of bottom currents, the occurrence of local interruptions in growth, variations in supply and deposition of ore minerals, i.e., facies conditions. The morphology and relative height of the submarine rises, and apparently the intensity of mixing and upwelling of water and shifts in the oxygen minimum (?) may also have been important.

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FAST STRUCTURAL ORDERING OF SMECTITES DURING ELECTRON DIFFRACTION STUDIES

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UDC 548.0:53

Smectite, an important clay mineral, is not easily susceptible to structural analysis. Smectites are characterized by a high degree of dispersion and disorganization of the relative position of 2:1 layers making up the structure. Normally, the layers are separated by loosely bonded water molecules and a small amount of exchange cations. Heating and saturation of the interlayer spacings by organic molecules can cause the spacing to vary broadly, resulting in a highly variable structure typical for smectites [2]. An effective method for structural studies in this case is x-ray diffraction [3, 6].

As objects of diffraction investigation, smectites appear as a one-dimensional sequence of two-dimensional lattices represented by the individual layers. The diffraction patterns contain fringes of two-dimensional diffraction hk and basal reflections $00l$. Despite the limitations of x-ray powder patterns, the expressiveness of the series of basal reflections, which is a succinct characteristic, and the possibility of controlling by it the effects of various smectite treatments, the x-ray method proved effective in describing structural dynamics of smectites [3, 6]. On the other hand, structural studies of smectites by this methodology could never reach the degree of detail obtained for other phyllosilicates, whose diffraction patterns contain sets of hkl reflections, representing a three-dimensionally periodic lattice (as in micas, kaolinites, etc.).

In 1976, in a study of potassium cation fixation during exchange reactions of a smectite (montmorillonite), Mamy and Gaultier [7] discovered a marked improvement of x-ray patterns after treating specimens with potassium salt solutions, rinsing the extruded cations of the exchange complex and subjecting the specimens to a series of hydration and drying (HD). Remarkably, in order to determine the effect more clearly, the authors recorded x-ray patterns from structures with photographic intensity registration. Modulation of diffusion fringes hk or even discrete diffraction patterns that appeared as three-dimensional hkl reflections was evidence of a relative ordering of the position of layers. However, it was only in [4] that this effect was used for a detailed structural analysis of smectites, made possible by the qualitative changes of the expressivity of diffraction patterns. To this end, the authors employed electron diffraction patterns from oblique structures, effective for these applications [1].

Interpretation of electron diffraction patterns from structures yielded important crystallochemical conclusions concerning the internal structure of 2:1 layers, and the regular position of layers in the artificially induced state of the mineral. It was determined that the relative position of tetrahedral and octahedral networks in a layer may vary for different dioctahedral smectites, depending on their composition, distribution of isomorphic substitutes, and genesis. In particular, a remarkable discovery was made that there are layers in which tetrahedral networks are tied only by an axis of the second order, although usually also tied to a symmetry center. Such layers can be interpreted as having vacant cis- and trans-octahedra. In addition, from the geometry and intensity distributions of reflections $02l$ and $11l$, determined after specimen treatment, it became possible to distinguish smectites with a uniform population of all octahedra by cations with a probability of 2/3 and varieties intermediate between the three forms of cation distribution in octahedra. This was the beginning of a new era of smectite studies, based on the possibility of obtaining previously unavailable valuable information on the detailed structure of layers.

We should note that potassium treatment of smectite [7], developed for study of the changes in the composition of the exchange complex, requires considerable amounts of mater-

Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 140-143, March-April, 1989. Original article submitted April 18, 1988.

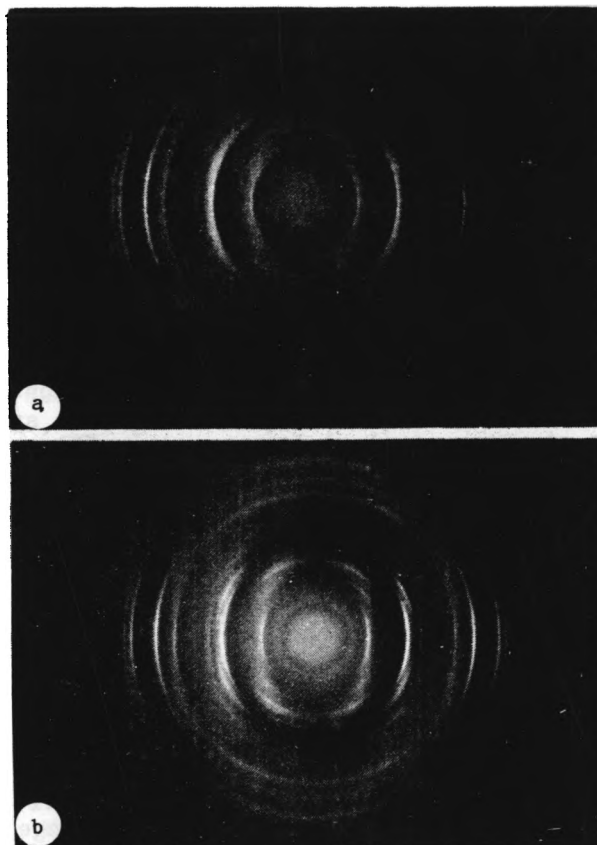


Fig. 1. Electron-diffraction patterns of bentonitic clay (specimen from the collection of G. A. Machabeli) before (a) and after (b) K-treatment, corresponding to the +14 effect.

ial, making each HD cycle too long and laborious. It may be acceptable for special fundamental investigations, but it is too cumbersome for diffraction-pattern monitoring of regular specimens in current analytic work in laboratories, especially when processing large systematic collections. In essence, the laboriousness of this procedure for diffraction experiments is excessive, because one is only concerned with the degree of structural ordering acquired by the end state of the specimen as compared with the initial stage. As a result, lots of material can be saved. The modified and facilitated procedure of structural ordering of smectites is particularly suitable for electron diffraction studies that require minute amounts of specimen and improve the effect of relative layer ordering by eliminating interlayer water molecules in the instrumental vacuum [1]. An efficient procedure for structural ordering of smectites for the purpose of an electron diffraction study is described in the present paper.

Description of the Method

The main idea of the method of structural ordering of smectites for electron diffraction investigation is one of using infinitesimal quantities of material sufficient for preparing electron diffraction preparations and combining two operations (saturating the specimen with potassium cations and performing HD cycles) in a single process. Instead of potassium salts (KCl , K_2CO_3 , etc.), a weak solution of KOH is used as the source of cations; instead of distilled water, the same KOH solution serves for swelling the structure. This eliminates rinsing salt solutions from specimens, because drying does not involve precipitation of crystals that could contribute to the diffraction pattern and interfere with interpretation of the structural changes of the smectite. Substitution of potassium for other cations of the initial exchange complex occurs during all HD cycles and is accompanied by progressive ordering of the relative position of layers. In addition, an alkaline medium is favorable for stabilizing the condition of smectites. During the procedure, potassium ca-

tions are fixed more completely, losing exchange capacity; the relative position of layers is ordered, and their bonds are strengthened, losing the capacity for divergence.

In practice, each potassium treatment of specimens is performed as follows [5]. Some 10-15 mg of dry specimen material is ground in a mortar to thin powder, then placed on the object glass. The first wetting with 0.01-0.1 N KOH solution is done by placing drops around the material which is at the center, so that the material can dissolve the drops and not fall apart. In the subsequent HD cycles a single drop is placed at the center of the precipitate. The specimen is dried under a powerful lamp or in a furnace at 100-120°C. The effect of structural ordering was achieved after 70-80 HD cycles; subsequent cycles did not result in any significant improvement of electron diffraction patterns. Each HD cycle takes ~3 min; the entire procedure takes up to 3-4 h. Dozens of specimens can be processed simultaneously, making this a highly efficient procedure.

Testing of the Method

The efficacy and speed of the method was tested at the Electron Diffraction Laboratory of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Academy of Sciences of the USSR; the following initial materials were examined:

- a. a large number of smectite specimens (more than 100) belonging to different genetic types from various deposits in the USSR and other countries (from the collection of G. A. Machabeli) whose diffraction characteristics were obtained within a relatively short time;
- b. smectite specimens, represented by a small quantity (unique museum specimens that could not be restored and should not be wasted; products of natural processes forming smectites as minor isolates, rare signs of mineral transformation effects, including smectites as products of intermediate or final phases, etc.); and
- c. specimens with the swelling component, represented as an impurity among other minerals or as part of mixed-layer formations, including hydromicas and rectorites.

The degrees of structural ordering varied. The structural ordering of specimens in the initial state and after treatment can be characterized by the features of ellipses I and II, observed in electron diffraction patterns; reflections 02 ℓ , 11 ℓ and 13 ℓ , 20 ℓ are distributed along these ellipses. The former reflections belong to the group with indices $k \neq 3n$; the latter, with $k = 3n$. Four cases were distinguished:

1. both ellipses (I and II) are diffuse and contain no discernible discrete reflections; they characterize objects as one-dimensional sequences of two-dimensional lattices;
2. separate reflections are seen in ellipse II, while ellipse I is diffuse, indicating a degree of ordering of structures in projection onto the plane ac ;
3. a modulation of intensities in the position of three-dimensional reflections is observed in both ellipses, as evidence of three-dimensionally ordered structures; and
4. all reflections are discrete, characterizing a structure with a well-defined unit cell.

The actual diffraction characteristics of the structural ordering are highly variable and include several intermediate forms, expressed as qualitative modifications toward greater clarity and contrast of these electron diffraction pattern features, or vice versa. The effect of specimen treatment (Fig. 1) can be characterized by two indices: one related to the initial state; the other to the final state (such as 12, 13, 23, and 44). A slight effect that cannot be expressed by a change in the numeric index can be indicated by $\pm$ signs (for example, 22).

The potential specific forms of structural ordering of smectites have been described in detail in [4].

The results for the specific materials investigated by this method will be reported in future publications, to be co-authored with collection and specimen owners.

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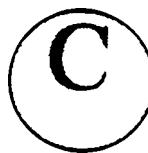
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